Illinois Institute
of Technology
UNIVERSITY LIBRARIES

AT 519
Parrot, Raymond D.
The synthetic manufacture of
 phenol

THE SYNTHETIC MANUFACTURE OF PHENOL

A THESIS

PRESENTED BY

RAYMOND D. PARROTT

TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

CHEMICAL ENGINEER

IN

CHEMICAL ENGINEERING

MAY 29, 1919

APPROVED:

H. McCormack

Professor of Chemical Engineering

Dean of Engineering Studies

Dean of Cultural Studies

ILLINOIS INSTITUTE OF TECHNOLOGY
PAUL V. GALVIN LIBRARY
35 WEST 33RD STREET
CHICAGO, IL 60616

- OBJECT -

I submit this volume on the Synthetic manufacture of Phenol to the Armour Institute of Technology as a thesis to obtain the degree of Chemical Engineer.

It is my intention to give a brief-as-possible, yet comprehensive and detailed dissertation on my experience and observations obtained while connected with the Phenol Plant of the New Port Chemical Works.

I will try to give a detailed discussion of the Chemistry of the manufacture, and of the operation of the plant. I will give pound, volume, and efficiency values for the individual steps in the manufacture which I know to be correct, but outside of rough estimates no gross tonnage figures will be submitted.

I intend to describe the layout of the plant and the apparatus and discuss some

28446

Digitized by the Internet Archive
in 2009 with funding from
CARLI: Consortium of Academic and Research Libraries in Illinois

http://www.archive.org/details/syntheticmanufac00parr

of the difficulties that came to my notice.

When I came to New Port (July 1917) the Phenol production was around 40 tons per day. In about nine months this production had increased from 40 to 60-65 tons per day. The bulk of the Phenol was being used for war purposes. About April it was decided the tonnage should again be increased, and truly it was, for in four months a beautiful new plant of capacity equal to the old one was in operation, adding enough tonnage production to the old plant production to make a total of about 130 tons per day.

It was in the "60-ton days" that the efficiency was highest and it is with this time that my efficiency figures deal.

The new plant was built in record time after much experience had been obtained in altering and rebuilding the old plant. Subsequently an ideal plant was the result. It is this plant that will be the subject

of my plant layout and it is of the old plant I will describe and discuss the difficulties.

Milwaukee, Wisconsin
December 15, 1919 Raymond D. Parrott.

CONTENTS

Page

Process - - - - - - - - - - - - - - - - - - 1

Sulphonation of Benzene - - - - - - - - - 4

Sulphonation Under Vacuum - - - - - - - - 17

Dennis-Bull Process - - - - - - - - - - - 20

The Conversion of Sulphonic Acid to Calcium Benzene Sulphonate - - - - 26

Oliver Filtration - - - - - - - - - - - - 31

The Sodation or Conversion of the Calcium Salt to the Sodium Salt - 44

Evaporation or Concentration of Soda Liquor - - - - - - - - - - - - - 48

The Fusion of Sodium Benzene Sulphonate With a Caustic to Produce Sodium Phenate (and Sodium Sulphite) - - - 54

The Fusion Room - - - - - - - - - - - - - 58

Fusion Room Operation - - - - - - - - - - 60

Some Difficulties of the Fusion Room - 69

Experimental Fusions - - - - - - - - - - - 76

The Liberation of Crude Phenol and the Recovery of Phenol in the Waste Liquor - - - - - - - - - - - - - - - - 94

CONTENTS

Page
Distillation of the Crude Phenol - - - 107
Treatment of Still Residues - - - - - - 116
Still Measurements - - - - - - - - - - - 119
Methods of Analysis and Control - - - 123
Organization - Methods - Layout - - - 148
Miscellaneous Data - - - - - - - - - - - 165

Blue-Print Plates

Facing Page
General Layout - - - - - - - - - - - - - 3
Sulphonation Chart - - - - - - - - - - - 6
Sulphonation Kettle Detail - - - - - - - 12
Vacuum Sulphonation Apparatus- - - - - - 18
Dennis-Bull Process - - - - - - - - - - 24
Oliver Vacuum Filter - - - - - - - - - - 32
Fusion Chart - - - - - - - - - - - - - - 56
Fusion Room Detail - - - - - - - - - - - 59
Experimental Fusion Charts - - - - -78 & 80
Separator - - - - - - - - - - - - - - - 95
Extractor Detail - - - - - - - - - - - -103

[illegible]

[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]

[illegible]

[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]

CONTENTS

Page

Badger Distillation Apparatus - - - - - - 111

Boiling Point Curve for Phenol - - - - 112

New Port Chemical Works - - - - - - - - - 151

Bird's Eye View - - - - - - - - - - - - - 153

Flow Chart - - - - - - - - - - - - - - - 154

- PROCESS -

The process of the Synthetic manufacture of Phenol was by the way of the sulphonation of benzene. The Synthesis consisted of six distinct and separate steps, the first five constituting fixed chemical reactions and the sixth or last step consisted of a mechanical procedure, distinct and particular as those that preceded.

They are as follows:

(1) The sulphonation of benzene to Monobenzene Sulphonic Acid.

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$$

(2) The conversion of the benzene sulphonic acid to calcium benzene sulphonate.

$$2\,C_6H_5SO_3H + Ca(OH)_2 \rightarrow (C_6H_5SO_3)_2Ca + 2\,H_2O$$

(3) The sodation or conversion of the Calcium Salt to the Sodium Salt.

$$(C_6H_5SO_3)_2Ca + Na_2CO_3 \rightarrow 2\,C_6H_5SO_3Na + CaCO_3$$

(4) The fusion of the sodium salt with Caustic Soda to produce sodium phenate as the main product and sodium sulphite as a by-product.

$$C_6 H_5 SO_3 Na + 2 Na OH \rightarrow C_6 H_5 ONa + Na_2 SO_3 + H_2O$$

(5) Decomposition of the sodium phenate with a mineral acid with the liberation of crude phenol.

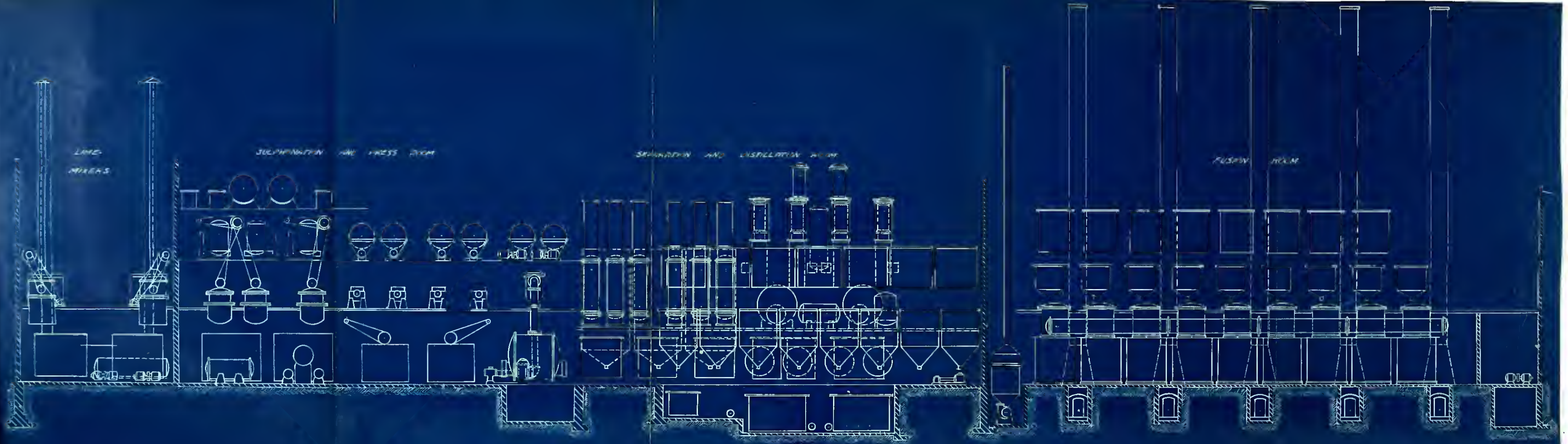
$$2 C_6 H_5 ONa + H_2 SO_4 \rightarrow 2 C_6 H_5 OH + Na_2 SO_4$$

(6) Distillation or purification of the crude phenol to the marketable product.

Each of these steps was beset with large and small obstacles which were more or less overcome by diligent observation and study in a comparatively short space of time.

A temperature of the sulphonation of benzene, the proportions of benzene and sulphuric acid, and the manner in which they were mixed, was simplified to a matter of routine operation.

Liming of the sulphonation and


LIME-
MIXERS
SULPHONATION AND PRESS ROOM
SEPARATION AND DISTILLATION ROOM
FUSION ROOM

·GENERAL - LAYOUT·

·SCALE · 1' = 3/32"·

conversion of the calcium salt to the soda salt gave little trouble. The filtration of the gypsum or calcium sulphate cake was solved mechanically, but there still remained to find a way, with the installed apparatus, to wash the cake efficiently. Perhaps the greatest difficulty of the soda salt operation came at this point. It received more than its share of attention and still the results fell short of those desired.

The mechanical operation of the fusion room had become routine. With careful attention (and not too great a rush for tonnage) on the part of the Operators, and with what knowledge of the process we had, good fusions were a common thing. With a little tutoring the Operators became expert-like in reading little signs and indications of a good fusion.

Anybody that could turn a valve or start a pump, and could read English was able to acidify the fusions. The recovery of the waste phenol and the distillation of the crude were easily performed after one had become thoroughly familiar with the apparatus.

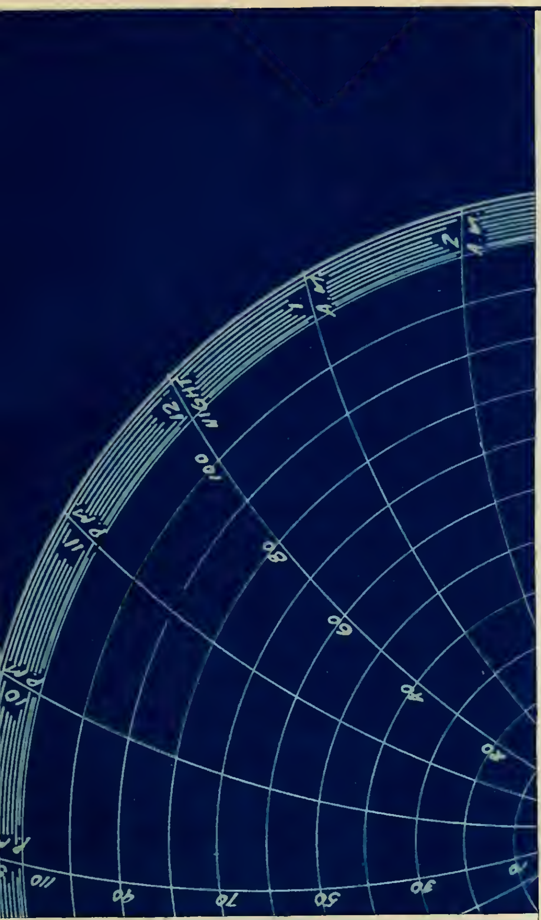
- SULPHONATION OF THE BENZENE -

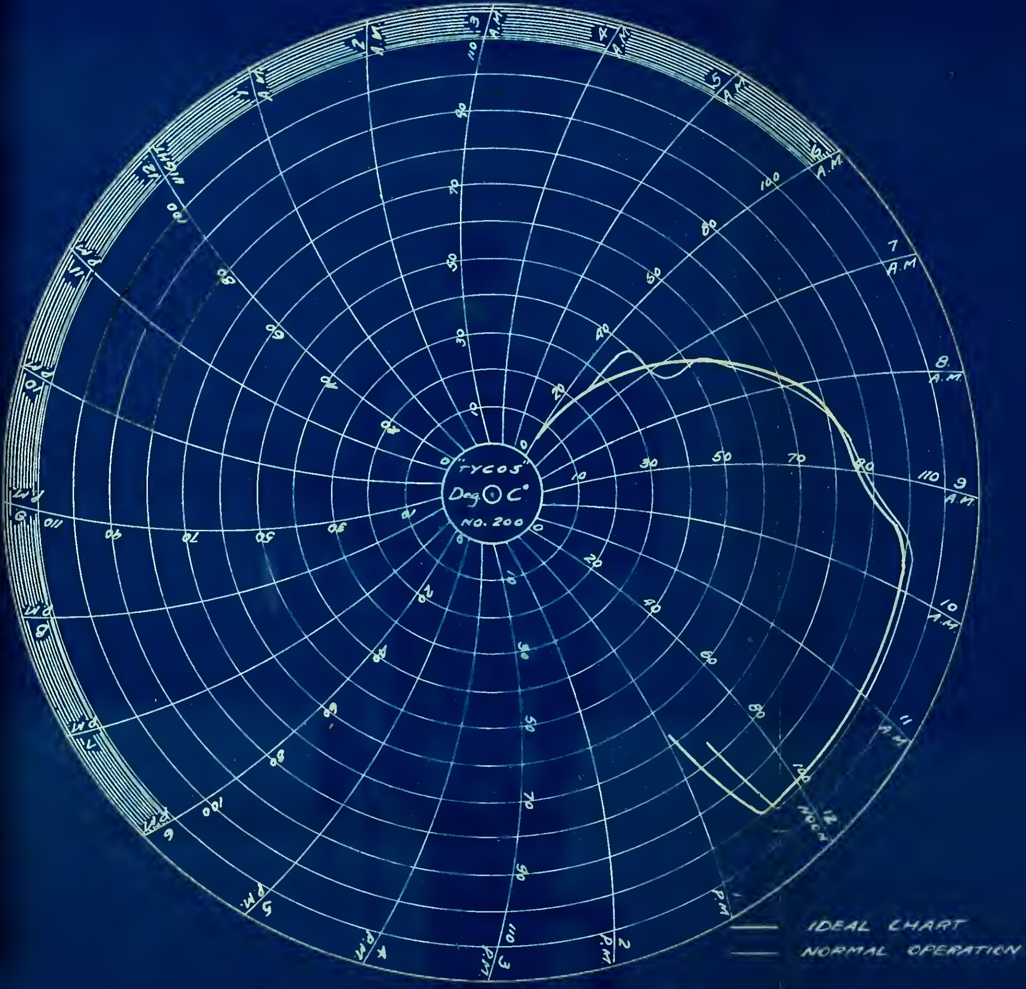
A "Sulphonation" having been dropped to a montejus, and the temperature in the kettle having dropped to 40° or 50° C. due to the cooling water running the while, the kettle was ready to be charged again.

Twenty-one hundred pounds of benzene (pure water-white) were dropped by gravity from a weigh-tank to the kettle. While the benzene was dropping, 4500 pounds of 102 percent sulphuric acid were made ready to charge from a weigh-tank. These weigh-tanks, which were similar, were located above the sulphonation kettle. The benzene was pumped with a Worthington double-acting steam pump to the benzene weigh-tank and the acid was blown with blow-egg and 60 pounds air pressure to the acid weigh-tank.

As soon as the benzene was all in the kettle, which took 15 to 20 minutes, the vents to the kettle and the benzene drop-lines were closed, and the agitator started.

The water was running all this time. This done, the acid was started dropping to the benzene. The heat of reaction of benzene plus sulphuric acid caused the temperature of the kettle contents to approach 80° C., with cooling water running full stream. The rate of feed was controlled in accordance with a temperature chart. The Operator attempted to follow the template or guide line (adopted through experimentation and experience) traced upon the chart beforehand. This made the rate of acid feed about 50 pounds per minute. If the needle on the temperature recorder overran the template line, the flow of acid was slackened a little, and if it did not come up to the line the flow was hastened. I have seen some operators make perfect charts, one right after another and then others miserably poor ones. Once in a great while a clock acted up when an agitator leg dropped off, and in such cases the best of operators could not follow the template line. Care had to be exercised to see that the acid


2 A.M.
1 A.M.
12 NIGHT
11 P.M.
10 P.M.
9 P.M.
100
80
60
40
20
110
90
70
50
30
10



·SULPHONATION·CHART·

R. D. Parrott '19.

was not fed too rapidly so as to cause excessive reaction and boil the benzene out upon the roof. Once 80° was reached (or a temperature greater than the boiling point of benzene) and the benzene had not boiled out, after all the acid had been added, there was little likelihood of its blowing to the roof. At the rate of 50 pounds of acid per minute, 1.5 hours would be required to make the charge. After this 1.5 (to 2) hours, the acid all in the kettle, and the temperature had reached somewhere around the 80° mark, the cooling water was shut off and exhaust steam turned in its place. This steam was required to raise the kettle contents to 100° C. This temperature was maintained to the completion of the "sulphonation", and that meant 1 to 3 hours on the average. After one hour a sample was taken out of the kettle and tested for benzene. A benzene content less than 2 percent was called finished and the "sulphonation" was ready to be dropped to a montejus below. Such a "sulphonation" was

a mixture of about 60 percent sulphonic acid and 40 percent spent acid. If the benzene content was greater than 2 percent the operation was continued. Samples then were taken about every half hour for a couple of hours. When less than 2 percent was noted the "sulphonation" was then ready to be disposed of. Generally at one hour the benzene content showed 7 to 10 percent benzene and in 1.5 hours less than 2 percent. There were exceptions to this, however. If, for any reason such as a low reading clock, low steam pressure, or a paddleless agitator, the charge in the kettle had been maintained around 90° or 95° instead of 100° C., the benzene was nearer to 20 or 30 percent unsulphonated. In such a case, especially if operation was in need of a "sulphonation", more acid was added, (to correspond to this 20 or 30 percent) say 900 - 1350 pounds and the "sulphonation" continued for another hour or perhaps two, in which time the benzene content dropped to 2 or 3 percent. If the percentage was greater than 2, and operation was

badly in need of the "sulphonation", it was dropped on order of the operating foreman. Too great a benzene content, however, not only lowered the efficiency but also hindered in the liming operation, the fumes often driving the operators away from the jobs and sometimes catching fire.

It has been found that benzene and sulphuric acid (concentrated) mixed in the theoretical amounts react to the point where the ratio of spent acid to water formed, is about 80 to 20 or to about a 58 percent "sulphonation". It is a well-known fact that concentrated sulphuric acid greedily attacks water to form a rather stable hydrate $H_2 SO_4 . H_2O$, and so as the water was formed in the "sulphonation" it was taken up by acid that was intended for the "sulphonation". This low figure of 60 percent is even greater than I would expect. For instance, from 78 pounds of benzene we should get theoretically 158 pounds of benzene sulphonic acid and 18 pounds of water, using 98 pounds of concentrated

sulphuric acid. This acid or 49 pounds would form 9 pounds of water, and as sulphuric acid and water combine in the ratio of 98 to 18 or 49 to 9, I would expect this 9 pounds of water to be taken up by the remaining 49 pounds of acid, but this is not the case and is probably due to the partial breaking up of the combination of acid and water by the high temperature of sulphonation (100° C.) along with the dilution by this same water and sulphonic acid, thereby freeing acid to the extent of increasing the "sulphonation" from 50 to 58 percent.

It was for the reason of only partial sulphonation, with the theoretical amount of acid that we had to employ 4500 pounds of 102 percent sulphuric acid or 4590 pounds of 100 percent acid, or about 40 percent excess of theoretical. This meant 1954 pounds of 100 percent sulphuric acid in excess of the theoretical amount of 2636 pounds of 100 percent acid:

$C_6 H_6 + H_2 SO_4 \rightarrow$
2100# 4590#

$C_6 H_5 SO_3 H + H_2O (+ H_2 SO_4)$
4252# 484# (1954#)

The efficiency of the average "sulphonation" was about 96 percent of theoretical, or 4060 pounds actual sulphonic acid instead of 4252 pounds were formed. About .5 percent of the benzene was converted to diphenyl-sulphone, $(C_6 H_5)_2 SO_2$. Instead of there being 1954 pounds of excess sulphuric acid in the final "sulphonation" mixture there was nearer 2050 pounds. Hence a final "sulphonation" showed roughly about:

$C_6 H_6 + H_2 SO_4 \rightarrow$
2100# 4590#

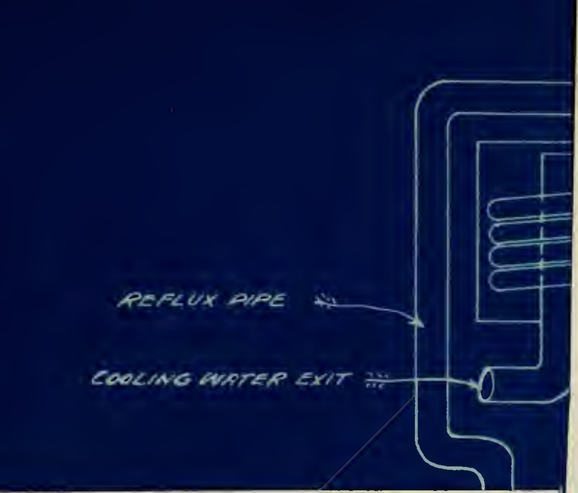
$C_6 H_5 SO_3 H + H_2O + C_6 H_6 + H_2SO_4$
2060# 475# 30# 2050#

The total acidity (sulphuric plus sulphonic) was equal to about 50 percent of the mixture by weight or 30 percent sulphuric and 20 percent sulphonic acid.

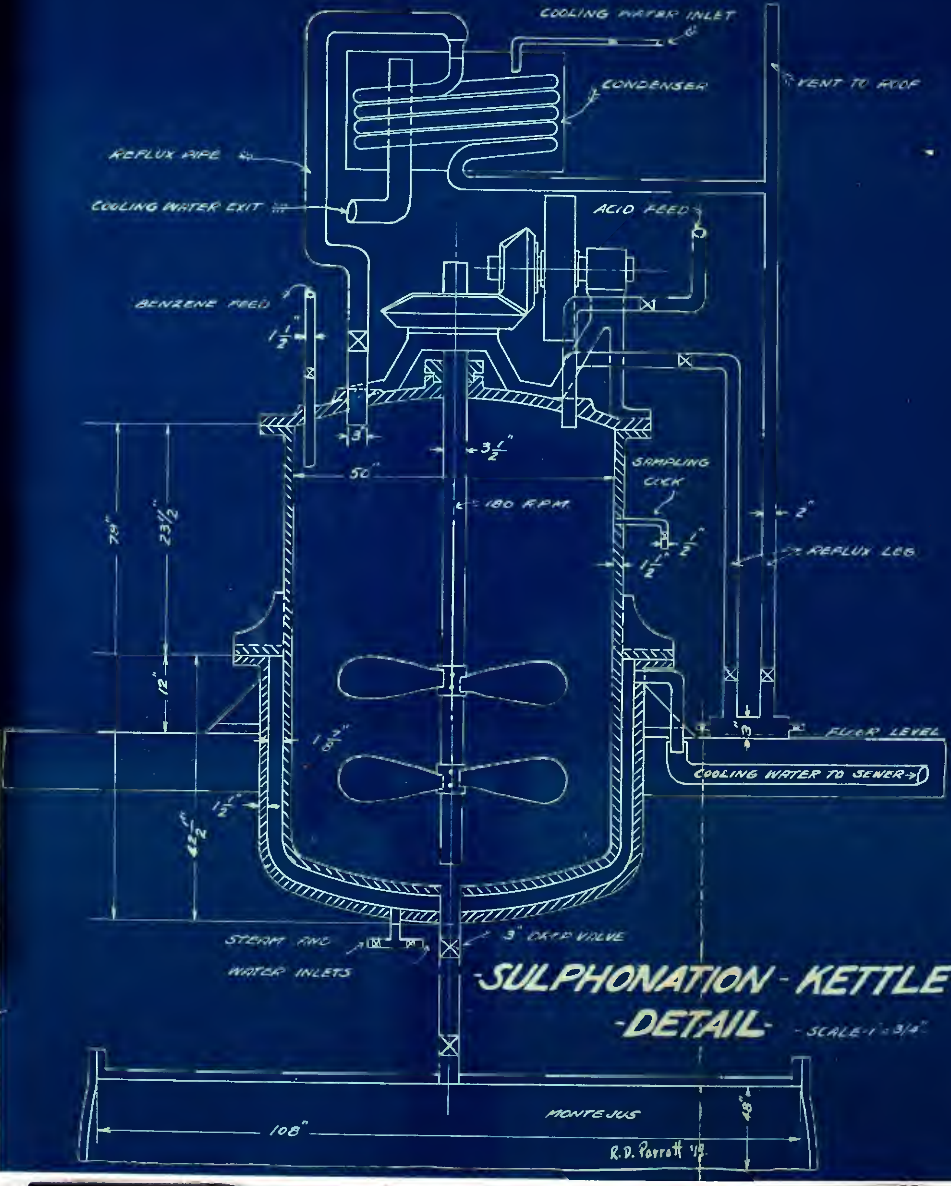
I think it would be safe to say with

careful charging and everything working smoothly about 20 to 40 pounds of benzene escaped through the vent to the atmosphere. If for any reason such as a "jam" in the operation a sulphonation had to be held in a sulphonator 15 to 20 hours, the efficiency was not so great. The sulphone increased and the sulphonic acid had a tendency to break up into benzene and sulphuric acid. This was especially true if the kettle vent to the roof became clogged and a slight pressure was formed in the kettle. This gave a pressure of steam which tended toward a reversible reaction. Laboratory results bore out the fact that a sulphonation completed in 5 to 6 hours was most efficient, in respect to both benzene and acid.

The apparatus used in this operation was probably standard of the country. A 630-gallon cast-iron sulphonator was used with centric or excentric agitation by means of a vertical shaft and horizontal paddles. The speed of the shaft was about 180 R. P. M. The kettle was jacketed so that water could be


REFLUX PIPE
COOLING WATER EXIT

condenser to the floor and thereby increasing the head or drop, this difficulty was minimized. If this condenser equipment had not


COOLING WATER INLET
VENT TO ROOF
CONDENSER
REFLUX PIPE
COOLING WATER EXIT
ACID FEED
BENZENE FEED
1 1/2"
3"
3 1/2"
50"
SAMPLING COCK
180 R.P.M.
2"
1/2"
1 1/2"
REFLUX LEG
74"
23 1/2"
12"
3"
FLOOR LEVEL
1 7/8"
COOLING WATER TO SEWER
1 1/2"
48 1/2"
STEAM AND WATER INLETS
3" DROP VALVE
MONTE JUS
108"
48"

-SULPHONATION - KETTLE-
-DETAIL-

- SCALE 1" = 3/4"

R.D. Parrott '19

applied for cooling or steam for heating. A vent was fitted in the benzene vapor line, and a sample cock in the body of the kettle.

A benzene reflux-like condenser was fitted to the kettle to care for the benzene vapors driven off by the violent reaction at the start of the "sulphonation". A surface area of 78 square feet served the purpose when properly applied. Plant pressure sufficed to throw the water to the coil tanks. Had this pressure been inadequate a pump was provided to act as a booster or do the work alone if necessary. A "U" bend or seal tended to syphon the condensed vapors of benzene back into the kettle. When the leg or "U" was first adopted it was made too short (about 8 feet) and the condensed vapors went largely to the roof and escaped instead of dropping to the kettle. By merely lengthening out the leg (from 8 to 16 feet) from the bottom of condenser to the floor and thereby increasing the head or drop, this difficulty was minimized. If this condenser equipment had not

been employed, the escaped benzene-loss to the roof would have amounted to 20 or 30 percent. I have been on the roof at the start of a sulphonation (when the short leg was in use) and have seen benzene come from the vent in a full stream and amount to perhaps 12 to 15 gallons.

Originally there was no leg extending to the bottom of the kettle on the inside, and the outside "U" was only 15 inches long. After some little agitation on my part this inside leg was installed in one of the kettles (No. 4). The blows to the roof (with the 8 feet head) were entirely eliminated and No. 4 kettle turned out more sulphonations in a shorter time than any other single kettle in the place, and more efficiently.

This could not be tolerated by "Outside" authority, because "he" could not see how an inside leg could remain any length of time and not be eaten away by the concentrated acid, even after it had been demonstrated very conclusively that such was not the case. Hence

the result was the outside leg (and no inside leg to the bottom) and the renewal of the blows to the roof. Since my time this No. 4 leg (on the inside) has been replaced and results obtained that verified my belief. It is my idea that the 2.5 pounds pressure and heat, which were in the kettle, had a tendency to force the incoming benzene from the "short inside leg" directly out and up the vapor vent, whereas the long leg allowed the incoming benzene to trickle below the acid and be partially sulphonated.

Every three or four days these outside legs had to be cleaned of "sulphonation" material. This was accomplished by blowing with steam, and the combination of valves on the outside leg gave any blowing combination necessary. A clogged leg meant a direct flow of benzene to the roof and that meant loss.

Generally during each day a valve or a length of pipe was eaten through by sulphuric acid and had to be replaced. A fitter and his helper attended to this matter.

A can containing a little soda ash or lime was set underneath the defective part and the remaining acid left in this part was allowed to drip. After the dripping had ceased the old part was replaced with a new part. An all iron valve fitted with special asbestos packing served about one month. Once a month or so a sulphonator agitator-paddle was eaten away, whence the top of the sulphonator was hustled off, the paddle replaced with a new one, and in four to five hours the kettle was in operation again.

-SULPHONATION RECORD-

No. Charged 37 | No. Dropped 35 | Date- I2-I6-'I7..

No.	Ket-tle.	No. Sulpho.	Benzene	Acid	Acid-Started	Acid All in.	Time-Dropped	Total Time	Percent Acidity	Percent Benzene Loss.
I	IO	I000	2I00	4500	I2:45A	2:20A	II:35A	I0:50	50:2	0.I4
2	3	I00I	2I00	4500	4:25A	6:50A	22:05R	8:40	5I.2	0.62
3	5	I002	2I00	4500	8:45A	I0:45A	4:I5P	7:30	52.5	0.I4
4	2	I003	2I00	4500	I2:20P	2:20P	6:50P	6:30	50.7	0.I4
5	II	I004	2I00	4500	2:35P	4:30P	9:40P	7:05	5I.4	0.83
6	I4	I005	2I00	4500	5:I5P	7:30P	I:I0A	7:55	48.0	I.50
7	6	I006	2I00	4500	8:55P	I0:45P	3:55A	7:00	49.2	I.80
8	7	I007	2I00	4500	I0:50P	I2:25R	5:50A	8:00	50.0	0.55

Average Benzene Loss - 0.7I %
Average Sulphone " - 0.5I %
Efficiency - - - - - -96.00 %

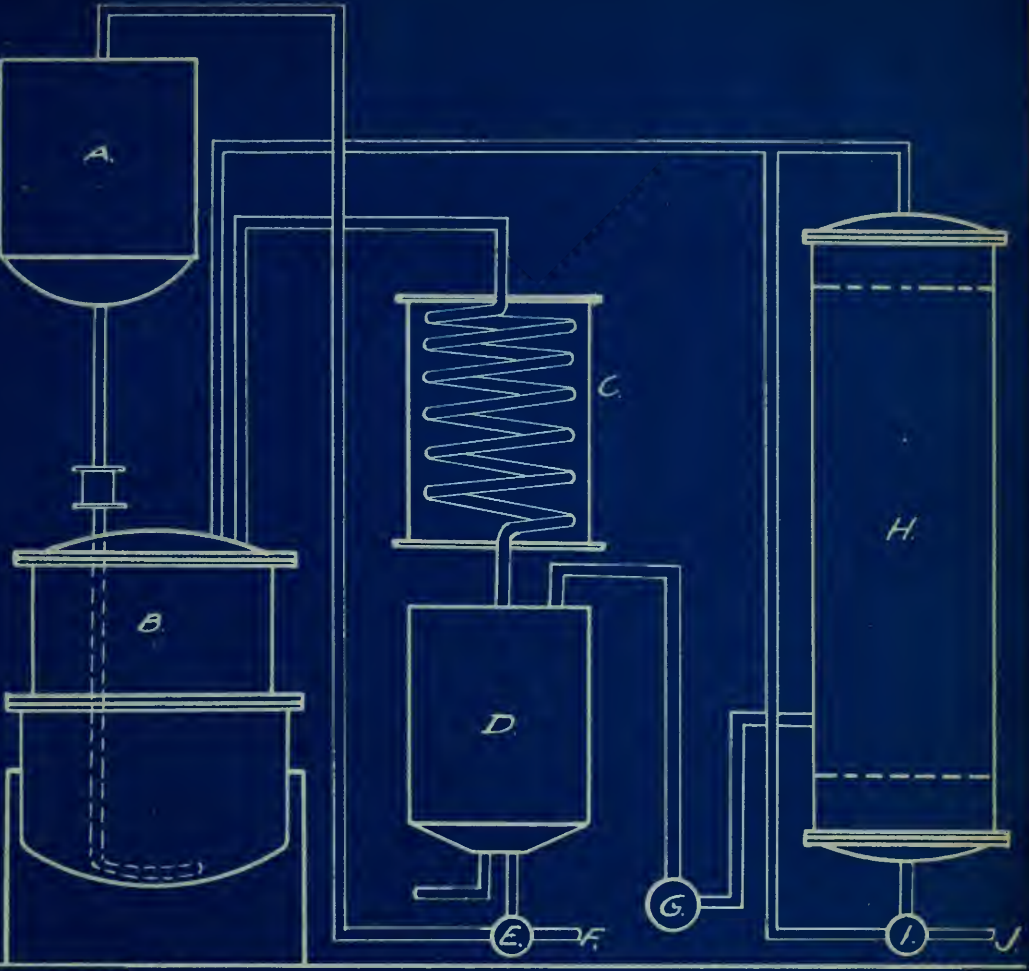
Shift No.	Lime	Soda Ash
I	6750	250
II	6000	300
III	5250	200
Total	I8000	750

- SULPHONATION UNDER VACUUM -

There has been developed a method of sulphonating under vacuum, a method that does away with the great excess of acid, (mentioned above and simplifies the liming process) if not eliminating it. It was not adopted at New Port because of the prospects of cessation of manufacture, and the burdensome litigation with which it was involved.

Two hundred gallons of 98 percent sulphuric acid are charged into a standard 600-gallon sulphonator with a gas fired furnace beneath. Straw oil is contained in the jacket and serves as the heat conductor. When the acid is all in the kettle, the benzene is fed to the sulphonator and the "sulphonation" carried to a 50 percent acidity in the usual way.

When this point is reached the vacuum pump is started and the whole sulphonation system (see drawing) is evacuated. When the gage shows 25 inches of vacuum, benzene is



A- BENZENE FEED TANK.
B- SULPHONATOR-
C- CONDENSER-
D- SEPARATING TANK.
E- BENZENE PUMP.

F- FROM BENZENE STORAGE.
G- VACUUM PUMP-
H- QUARTZ FILLED CIRCULATING TOWER-
I- ACID PUMP-
J- FROM ACID STORAGE-

-VACUUM - SULPHONATION- -APPARATUS-

R.D. Parrott '19.

allowed to feed from the gravity tank (A) and the flow regulated such that the vacuum is 20 or 21 inches. The temperature of the kettle contents is raised to 150° C and held there.

The vacuum is left on the system for about 1.5 hours and is then released, and the water collected in the tank (D), drawn off. More benzene is then run into the kettle to use up the concentrated acid (freed of water). The sulphonation is continued for an hour after which time a vacuum is produced again. The process of alternate evacuation and sulphonation is continued for an hour after which time a vacuum is produced again. The process of alternate evacuation and sulphonation is carried on 'till the final acidity of the mixture is about 30 percent or 3 percent sulphuric acidity. The time to bring the mixture down to a residual acidity of 3 percent sulphuric acid is about 20 hours.

About 150° C. was found to be the best temperature for the final stages of the sulphonation. A higher temperature increased

the formation of sulphone. 180° C. is not too high for the original evacuation and sulphonation.

The greater the capacity of the vacuum pump and the greater the quantity of heat applied, the sooner the "sulphonation" will be completed, as the main object is to drag the water away from the acid to make it concentrated so it can do "sulphonation work". To do this you must pass 10 times as much benzene through the cycle as you get water off, and the hotter the kettle contents are, the easier the water comes off, and the higher the vacuum the more benzene you can pass through the sulphonator.

The sulphuric acid tower is to catch the benzene vapors that go through the pump, partial sulphonation taking place here. This acid is put into the sulphonator for the next run and fresh acid put in its place.

- DENNIS-BULL PROCESS -

The following is a part of a paper by A. G. Peterkin of the Barrett Company, (Chemical and Metallurgical Engineering, September 1, 1918, page 258). He describes the new Dennis-Bull Process for making benzene sulphonic acid. I understand that the Barrett Company are or were some time ago turning out about five tons of phenol per day by this process of sulphonation.

"Some two years ago Professor L.M.Dennis (U.S.Patents,Nos. 1,212,612, 1,211,023, 1,228,441 and 1,229593) of Cornell University discovered that although the solubility of pure sulphonic acid in benzol was negligible, benzol would take up from the mixture of sulphuric and sulphonic acids 2 and 3 percent of its own volume of the sulphonic acid. In working out this idea it occurred to Mr. Hans Bull (U.S.Patents,Nos. 1,247,499 and 1,260,852) of that company that the sulphonation

could be made simultaneously with the extraction. These ideas have been utilized in the evolution of an extremely simple process which not only saves 90 percent of the excess sulphuric acid as a spent acid containing 70 to 77 percent H_2SO_4, but eliminates a good percentage of labor, all the lime, and substantially reduces the deplorable cost of repairs, due to the many moving parts of the old installation.

"The process will be easily understood from the Chart. The vessels 1, 2, 3 and 4, so-called "extractors", contain at rest a layer of a solution of sulphonic and sulphuric acids of varying proportions. The benzol passes continually upward through this series of extractors, the vessels being under a pressure equivalent to the head of benzol. The distribution of the liquid in fine bubbles is effected by means of perforated branch pipes. After the passage of the benzol for a certain length of time, the solution in No. 1 is free from sulphonic acid and consists of

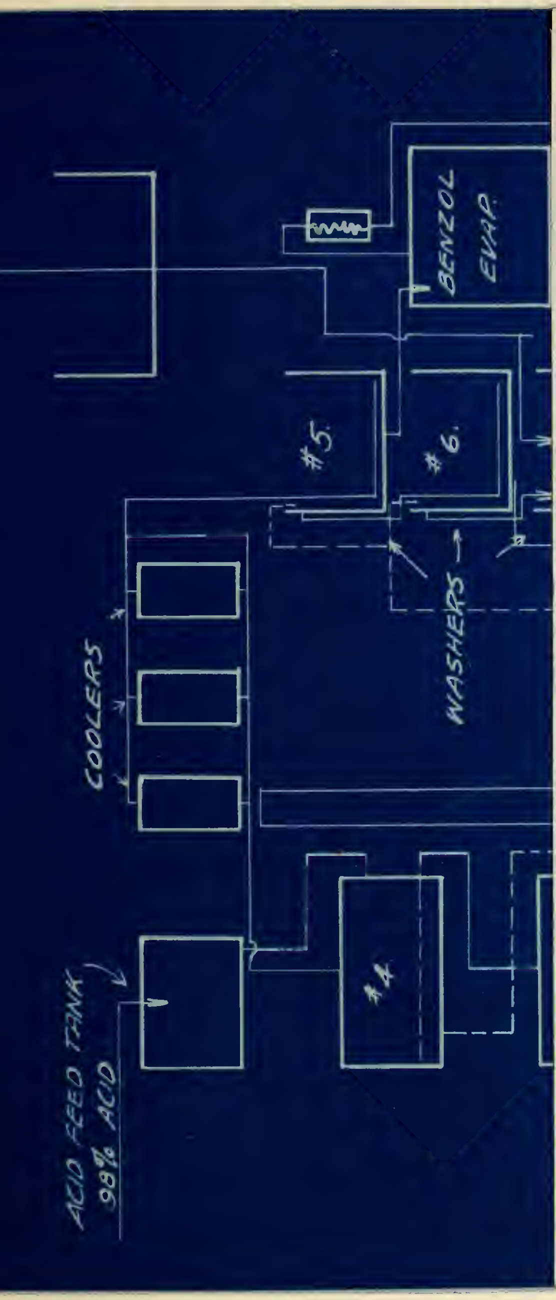
77 percent $H_2 SO_4$. When this has been accomplished, the so-called "spent acid" is withdrawn. The solution in No. 2, which probably contains 10 percent of sulphonic acid is dropped into No. 1. The solution in No. 3, which contains probably 25 percent sulphonic acid is dropped into No. 2, and the solution in No. 4, which contains probably 40 percent sulphonic acid is dropped into No. 3.

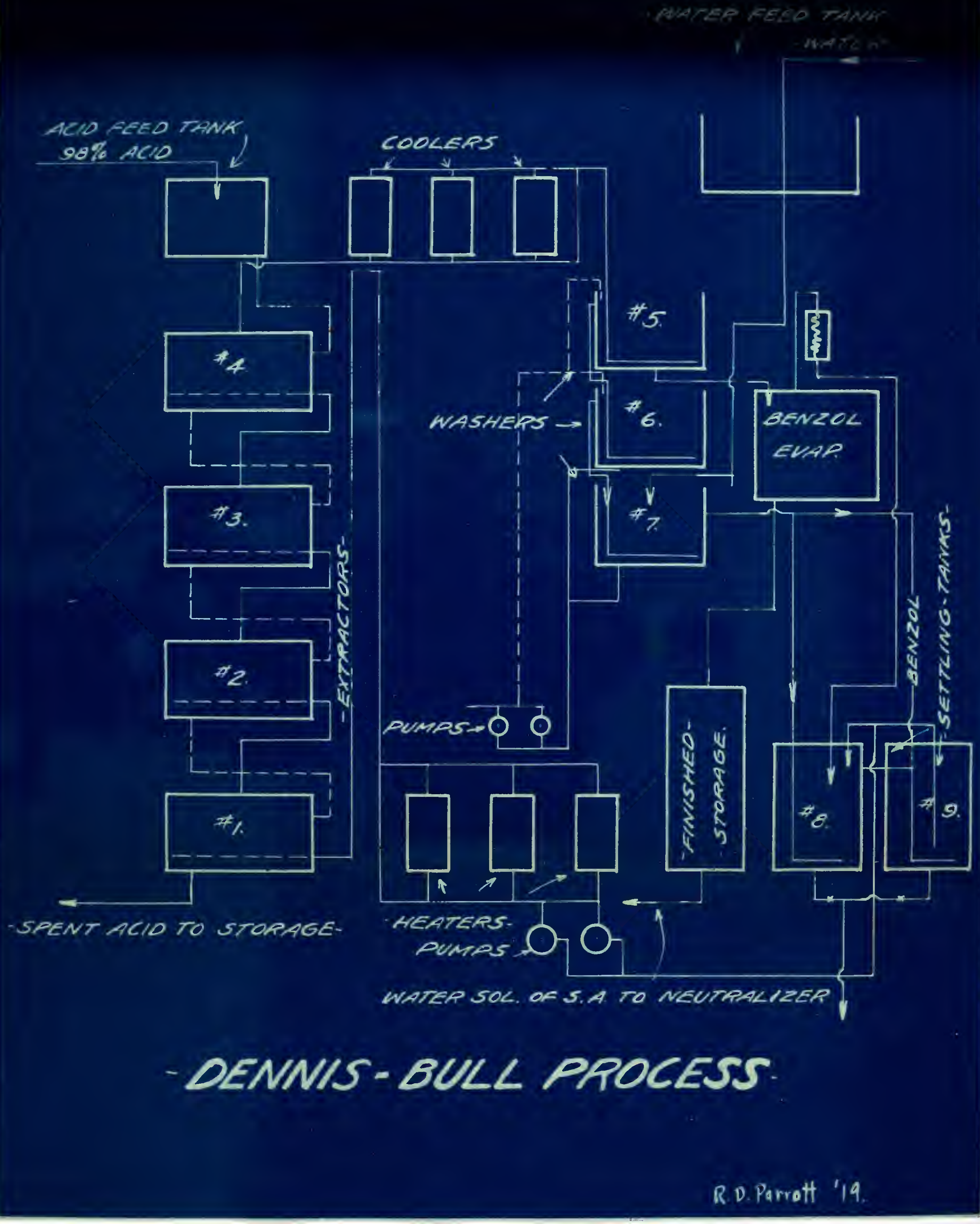
"Into No. 4 is then slowly introduced a charge of 98 percent sulphuric acid. The flow of benzol is not interrupted at any time. Sulphonation takes place almost immediately and the volume of the benzol flowing through, approximately 200 gallons per minute, is so great as to effect almost instantaneous removal of the heat of reaction. The benzol is maintained throughout at a temperature of 50° C. by heaters at the bottom of the system and coolers at the top.

"After passing through the coolers, the benzol, which will contain approximately 2 percent sulphonic acid, passes successively

through the washers, 5, 6, and 7, containing water. The benzol falls from one vessel to another by gravity, there being no pressure on this part of the system. The sulphonic acid remains in the water and the benzol leaves the last washer entirely relieved of its burden. It is passed to large settling tanks where the rate of flow is slowed down to such an extent as to allow the sulphonic acid solution, carried in suspension, to settle, and from these tanks flows to the pump and is forced through the heaters to the extracting system once more.

"When such an amount of sulphonic acid has been deposited in Washer No. 5 as to bring it to the strength desired, it is removed to an evaporator and the solution from Washer No. 6 pumped to No. 5, and that from No. 7 to No. 6. Fresh water is put into No. 7. A water solution of sulphonic acid can be obtained containing 60 percent, or even more, sulphuric acid and containing also about 2 volumes percent of benzol in solution. The


BENZOL EVAP.
#5.
#6.
WASHERS
COOLERS
ACID FEED TANK 98% ACID
#4


WATER FEED TANK
-WATER-
ACID FEED TANK
98% ACID
COOLERS
#4
#3
#2
#1
-EXTRACTORS-
#5
#6
#7
WASHERS
BENZOL EVAP.
BENZOL
-SETTLING-TANKS-
#8
#9
PUMPS
-FINISHED-STORAGE.
-SPENT ACID TO STORAGE-
HEATERS-
PUMPS
WATER SOL. OF S.A TO NEUTRALIZER

-DENNIS-BULL PROCESS-

R. D. Parrott '19.

The benzol is removed by evaporating a small percentage of the water. The solution of sulphonic acid is then neutralized, either by the carbonate solution from the phenol blowers or with the solid sulphite of soda. The sodium benzene sulphonate obtained contains some 5 or 6 percent of sodium sulphate, due to the solubility of sulphuric acid in the benzol solution of sulphonic acid (one part sulphuric to twenty parts sulphonic).

"ADVANTAGE OF THE PROCESS

"The advantages of the process are obvious. The initial cost of the plant is about 50 percent of that of the old style plant, which it displaces. Moreover, it runs practically without attention and requires from one-third to one-fourth the number of laborers. Taking for granted complete extraction of the sulphonic acid, which proves quite possible, and a removal of the benzol from the water solution of sulphonic acid, the losses possible are confined to mechanical causes, that is, either leaks or evaporation. The yield under

the old process, from benzol to sodium benzene sulphonate is about 90 percent. The new process makes easily possible a yield of 98 percent, leaving the mechanical losses out of consideration. The formation of disulphonic acid and of sulphone is negligible. The operations: (1) discontinuous sulphonation, (2) liming, (3) filtering, and (4) evaporating, involving complex machinery and many moving parts, have all been displaced with the one simple and continuous operation, extraction and sulphonation going on simultaneously, the only moving parts being two small pumps. The spent acid is concentrated to 93 percent and used repeatedly --------------------."

THE CONVERSION of the SULPHONIC ACID to CALCIUM BENZENE SULPHONATE.

After a sulphonation showed less than 2 percent benzene, it was dropped to a montejus below, and from there it was blown to a gravity tank above the lime tubs. From here it was dropped to a lime tub and the excess sulphuric acid was neutralized and the sulphonic acid was converted to the calcium salt.

A lime tub was ready to receive a sulphonation when it contained about 12 inches, or half the required amount of hot milk of lime, and the air agitation was on. A trap-like door in the cover of the tank was closed to within about 2 inches of being shut. (If it were closed all the way it would be blown open, but as it was fixed it afforded a good draft from the lime room to the stack.)

With the lime in the tub and the air on, the "sulphonation" was dropped at a rate which the operator saw fit. As the "sulphonation"

with its 50 percent excess free acid, hit the hot lime, great volumes of steam and benzene vapors poured up the stack and through the 2-inch crack at the trap door. If the sulphonation was dropped too fast the contents would boil over the top of the tub. After 5 or 6 minutes the steam and benzene vapors slackened, which indicated the free lime was decreasing or perhaps was all used up. At this stage more lime was added (from the mixers above) simultaneously with the "sulphonation" from the gravity tank. Toward the finish of this liming operation the operator tested the tub contents with a squirt of phenolphthalein from a bottle. "White indication" told him acid was still present, but after a few more tests he got his telltale pink test from excess lime, and alkalinity. In 15 to 20 minutes the liming was complete, the excess sulphuric acid had been neutralized and the sulphonic acid converted, and any benzene present, boiled off.

Now 10 to 12 inches of waste sulphite-sulphate liquor were added to the

limed sulphonation to about 85-95 percent conversion of calcium salt to sodium salt. Ten minutes of agitation to allow this waste liquor to react and the liming was ready to be filtered.

$2\ C_6H_5SO_3H + Ca(OH)_2 \rightarrow$

4252# 1456#

$(C_6H_5SO_3)_2Ca + 2\ H_2O$

4763# 945#

$H_2SO_4 + Ca(OH)_2 \rightarrow$

1954# 1476#

$CaSO_4 \cdot 2\ H_2O$

3430#

The 27-29° Be'. Waste liquor analyzed 23-25 percent sodium sulphate and 5-7 percent sodium sulphite, and weighed 10.4 pounds per gallon. It contained a small amount of phenol (.5 percent) and was highly colored from decomposition products of the fusion. 12 inches of liquor or 78.5 cubic feet (78.5 x 7:5 x 10.4) equaled 6122 pounds.

6122 X .23 → 1408# Na_2SO_4

6122 X .07 → 430# Na_2SO_3

$(C_6H_5SO_3)_2Ca + Na_2SO_4 \rightarrow$

3512# 1408#

$2\,C_6H_5SO_3Na + CaSO_4 \cdot 2\,H_2O$

3570# 1705#

$(C_6H_5SO_3)_2Ca + Na_2SO_3 \rightarrow$

1207# 430#

$2\,C_6H_5SO_3Na + CaSO_3 \cdot 2\,H_2O$

1280# 587#

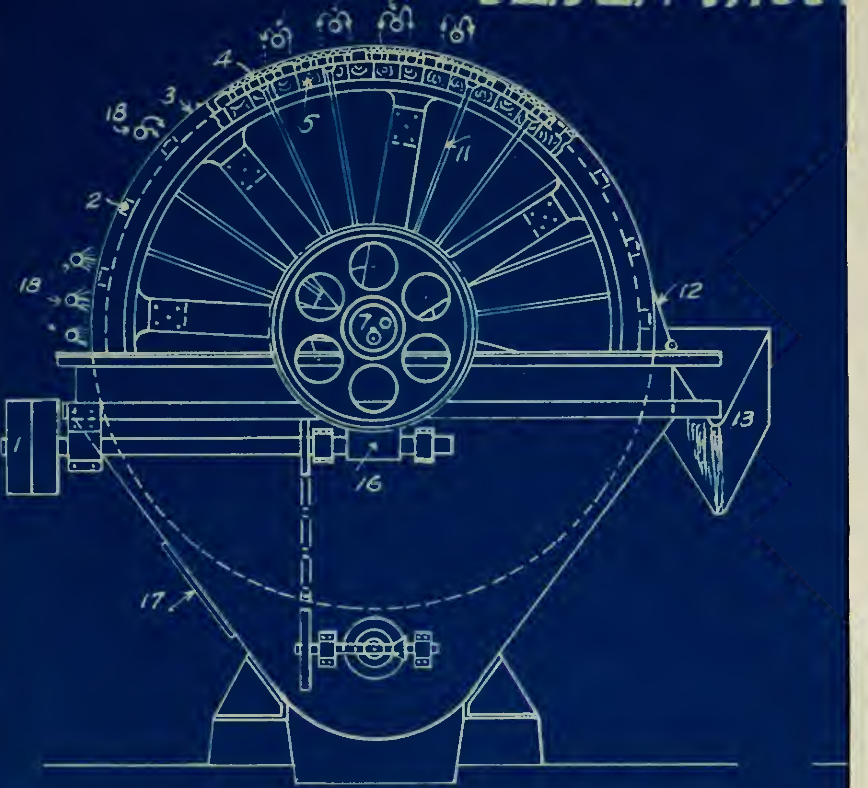
The lime tub was a plain wooden tank 10 feet in diameter and 8 feet deep, covered over. The cover (which was tight) was provided with a trap-like door about 2.5 feet on a side. The tubs were fitted with wooden vent stacks creosoted inside, and air agitator pipes. These pipes were 3/4 inch brass, perforated at the lower ends and extended to the bottom of the tub. These perforations were wound or wrapped over with strips of burlap and bound with wire. This covering kept out the sediment which otherwise would have clogged the holes.

The limed sulphonation was immediately

pulled, while hot, through a valve in the bottom of the tub by a centrifugal pump of ample size, and forced to the Oliver filter presses above. The tub and pipe lines, after the contents were pumped out, were well steamed to remove any remaining residue.

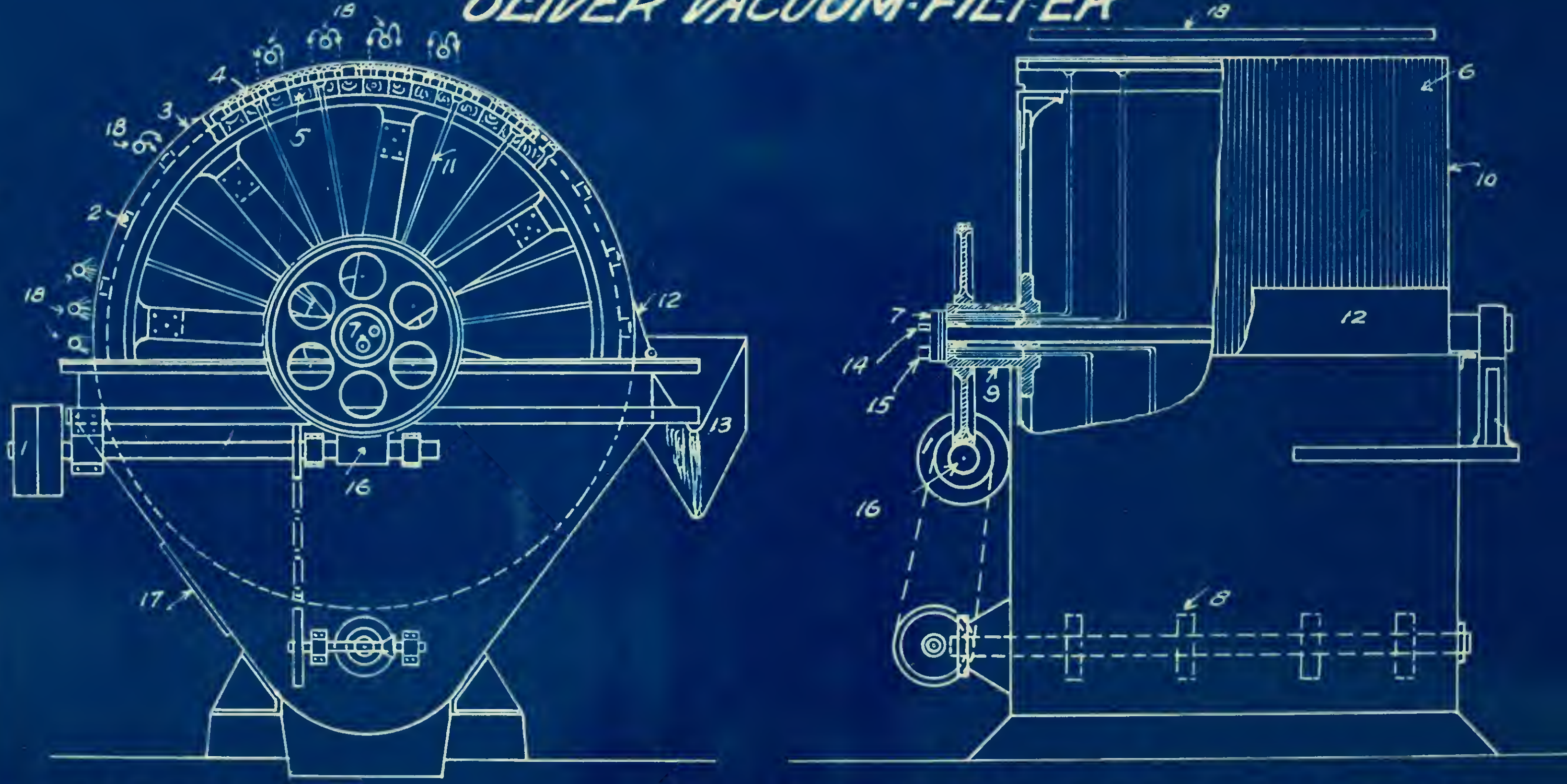
- OLIVER FILTRATION -

The Oliver Filter consists of a revolvable drum or cylinder with open ends, mounted on a horizontal axis with the lower portion submerged in a tank containing the material to be filtered. The surface of the drum is divided into 24 sections running parallel with the axis of the drum. These sectors are covered with a 5-mesh screening which acts as a background for the canvas. The latter is protected on the (other side or) outside by a wire winding of 1/16 inch wire and 9/16 inch pitch. Each section is connected by two pipes which are in turn connected with an automatic "headvalve". This valve performs in such a manner as to apply a vacuum at the canvas for a portion of a revolution for sucking cake and liquor, and then air for a part of the remaining portion of the revolution for the purpose of blowing the washed cake loose as it approaches a scraper. A mechanical agitator and also a blast of air in the bottom of the


18
4
3
18
5
11
2
18
7
12
13
1
16
17

1- FILTER DRIVE PULLEYS.
2- SECTION DIVISION STRIPS
3- FILTER MEDIUM
4- SCREEN BACKGROUND
5 WOODEN DRUM STAVES.
6- WIRE WINDING
7- AUTOMATIC VALVE
8- AGITATORS
9- A
10- F
11- V
12- S

OLIVER VACUUM-FILTER


18
18
4
3
18
5
11
2
18
12
7
1
13
16
17
18
6
10
7
14
15
9
12
16
8

1- FILTER DRIVE PULLEYS.
2- SECTION DIVISION STRIPS
3- FILTER MEDIUM
4- SCREEN BACKGROUND

5 WOODEN DRUM STAVES.
6- WIRE WINDING
7- AUTOMATIC VALVE
8- AGITATORS
17- MAN HOLE

9- HOLLOW C. I. TRUNNIONS
10- FILTER DRUM
11- VACUUM PIPES.
12- SCRAPER
18- WASH WATER SPRAY PIPES

13- FLUSH TROUGH.
14- STEAM BLOW INLET
15- VACUUM CONNECTION.
16- WORM DRUM-DRIVE.

R. D. Parrott '19.

tank provide for a uniform cake. A filtrate receiver is provided which empties into the soda conversion tubs below. The cake goes to a gutter and from here it is flushed to the dump by way of a canal for the purpose.

Oliver operation on paper was simpler than in actual practice. The quality of cake, the thickness of cake, and the correct amount of wash water and its application were the important items in Oliver operation. The material tank had to be kept full in order that the cake did not become free, vertically, of the liquor level too soon. If such was the case the cake sloughed or dropped off from its own weight and cracked for the lack of wash water which was not applied so low in the tank.

Best Oliver operation was to keep the tank full, regulate the vacuum so that about 3/4 inch cake was pulled, and apply wash water gently so as not to cut the cake. This necessitated the continual adjustment of the vacuum valve as not all of the cakes were of the same quality and the vacuum was not of

constant value. Generally speaking however, a single limed "sulphonation" maintained its regulated cake, but the following "sulphonation" would take more or less vacuum, depending upon the quality of the cake. By quality of cake I mean porosity and texture.

An attempt was made to regulate the thickness of the cake with the head valve alone, by cutting short the usual or standard suction travel. This did not prove satisfactory because the different filters did not all behave alike, and the quality of cake was too variable.

Wash water was applied by 3 pipes of 8 spray-nozzles each, at the back of the drum, and 5 one-inch pipes, with 3/16 inch holes spaced 1 inch apart, located - 4 at the top and 1 midway between the 3 spray-nozzles at the back and the above mentioned 4. These water pipes were about 4 inches off the drum with the 3/16 inch holes away from the cake. The water issued from these holes with a force great enough to throw it up 2 inches

in the air and allow it to drop gently upon the cake. These drilled 1-inch pipes served better for washing than did the sprays, as the latter cut the cake and the former did not. The wash water was maintained at 75-85° C. and 5 pounds pressure, and instead of air 30 pounds of steam were used on the blow. This wash water consisted of the condensate and condenser water from the evaporators brought up to 75-85° C. by sending it through a special heater for the purpose. If the water was heated to too great a temperature it was difficult to maintain a cake on the filter, because as the hot wash water entered the vacuum pipes it flashed into steam due to the reduced pressure, and this caused the vacuum to drop, and in turn the cake to slough or break loose.

When I first went to the plant the Olivers were not working exceptionally well. They were sloppy and needed cleaning often. The little vacuum air pipes and head-valves were clogged and needed steaming, and in some

cases scraping out. An analysis of this material in the pipes showed about 50 percent of diphenyl-sulphone, along with a little lime and ferric hydroxide. A little experiment carried out by myself in the laboratory brought about the change of air to steam blow on the canvas. The following is a copy of my report:

"A sample of limed "sulphonation" going to the Olivers was divided into two equal portions, one was heated to boiling and the second was cooled to 24° C. (tap temperature). Both portions were filtered through two thicknesses of qualitative filter paper. Both filtrates were then cooled to (tap temperature) 24° C.

"The filtrate of the hot portion showed a precipitate of sulphone upon being cooled. The filtrate of the cold portion showed no precipitate.

"As sulphone is insoluble it might appear that it is held in a finely divided state of suspension or in a colloidal (or otherwise) condition in the hot. In this

condition it is able to pass through the filter into the filtrate. This hot filtrate upon being cooled gives up the sulphone as a light flaky precipitate.

"In the cold portion, then, they are present as a precipitate and are held back by the filter from going into the filtrate.

"This means that the material to the Olivers when hot contains the sulphone in a condition to pass the filter and when cold in a condition to be held by the filter."

August 1918.

It was plain then that the liquor had to be hot or cold to either pass the sulphone or to hold it. If the liquor was cooled calcium and sodium benzene sulphonate would tend to crystallize out and it would be impossible to wash these salts out of the cake. It was then decided to maintain the system as hot as possible and pass the sulphone. To aid in this decision the air blow was replaced by the 30-pound steam blow

and steam agitation in the bottom of the tank replaced the air agitation.

Now instead of finding the sulphone in the vacuum pipes and head-valves, it is found floating as a soapy, sudsy foam on the surface of the converted soda-liquor.

Often the cake on the press became streaked, leaving the canvas bare in spots and loaded in others. These bare spots soon became baked by the steam and the pores in the canvas became absolutely closed. Once a canvas got in this condition it was little better than none at all.

When a press got this way it was shut down and scrubbed by hand with wire brushes. This scrubbing did some good to the canvas but no good to the wire screening beneath, which rapidly became clogged. It was then proposed and adopted, to shut down a press every 8 hours and scrub it before it became streaked and the pores were clogged and baked tight. This practice lengthened the life of the canvas. At intervals the

screening was removed and cleaned free of lime and foreign matter.

A streaked press was due to many causes, two of which were difference in quality of cakes and cutting of the cakes by the wash water as already mentioned. A too great wash pressure was sure to cut the cake.

I have seen canvas a little over 8 hours old that was in a worse condition than canvas 60 hours old, which was the average life of a well-handled canvas. After 60 hours a canvas became rotten and eaten and could not be scrubbed further without puncturing.

Limings varied greatly. Some produced a heavy porous cake, others a light powdery-like cake. If a "sulphonation" was pulled as soon as it was limed, the cake was hot, thick and heavy, yet porous. These cakes washed well and filtered rapidly. But if for some reason a limed sulphonation was allowed to stand idle and become cold, the air agitation being on the while, the cake became

light in weight and granular, and filtered slowly, and the cake was invariably thin no matter how great the vacuum. Also if a liming became cold the calcium and sodium benzene sulphonate crystallized out and a poor and inefficient wash at the press was the result.

An attempt was made to produce a good cake by dropping a "sulphonation" into an excess of milk of lime. The acid hitting the ever present excess lime formed a heavy cake. These "sulphonations" if pulled immediately, and while hot gave a good cake, but if allowed to cool and agitate, the cake was thin and granular. Also too much steam was generated in the lime tub so that method was abandoned.

A liming consisted of about 2250 gallons of 25° Be'. liquor. The above with the cake taken out approximated 1350 gallons of 15° Be'. liquor. With 1200 gallons of wash water there was a total volume of 2550 gallons of 8.5° Be'. filtrate liquor. This

meant that one gallon of 15° Be'. liquor was diluted to 1.9 gallons of 8.5° Be'. filtrate liquor.

3430 pounds of $Ca SO_4 . 2 H_2O$ + 1705 pounds of $Ca SO_4 . 2 H_2O$ + 587 pounds of $Ca SO_3 . 2 H_2O$ + 78 pounds of insoluble matter in the lime gave 5800 pounds of cake to the Olivers. The sludge which went over the scraper was about 1/2 water and 1/2 cake or correctly 48 percent water and 52 percent solids. Therefore 5570 pounds or 670 gallons of water were carried off with the cake.

The soda salt loss on the Olivers was from 1.5 to 2.5 percent of the Oliver cake or 87 to 145 pounds of soda salt. With a poor wash the loss was 200 to 300 pounds (or greater) of soda salt.

Several determinations for the percentage of insoluble solids (in water) gave 26 grams of solids obtained from 100 grams of well washed feed material or 26 percent insoluble solids - theoretically I get

$\frac{5800}{225 \times 8.33 \times 1.21}$ = 25.6 percent insoluble solids.

25° Be'. -------------------- = 1.2083 SP.gr.

2250 gals (1.2083) ------------- = 22,650 pounds.

22,650 = Total weight of liming .

22,650 X .26 ---------------- = 5,889 pounds.

5,889 + (4845 X .95) = 5889 + 4603 = 10491 ".

10491 ÷ 22,650 -------------- = 46.3% total solids.

Therefore -

Mother liquor - = 25° Be'. - (2250 gals.)
Total Solids - = 46.3 percent
Soluble " - = 20.3 "
Insoluble" - = 26.0 "

Using 6 presses (and washing one in its turn) or actually using 5 presses all the time and averaging 40 "sulphonations" per day (24 hours) during 22 days, we get the following figures for one press for (24 hours) one day.

Filtered limings - - - - - - -	8.0
Mother liquor, gallons - - - -	18,000.0
Wash Water, " - - - -	9,600.0

Dry Cake, pounds - - - - - - - 46,400.0

Wet Cake, " - - - - - - - 90,960.0

Soda Salt Loss, lbs.(142x8) - 1,136.0

Steam pressure on canvas
and agitation - - - - - 30 pounds

Size and No. of canvas - "Oceanic Cotton Duck" #12, (104 yards per rool). 17'6" lengths used, weighing 9.5 to 10 pounds each.

Wire screen (canvas background) 5 mesh. Binding wire 1/16 inch diameter and 9/16 inch pitch.

Spray equipment - 4,1-inch pipes above and one amidship with 3/16 inch holes spaced one inch apart, and 3 2-inch pipes with 8 standard nozzles each.

Vacuum - 20-22 inches mercury.

Temperature of wash water - 75-80° C. and 4-5 pounds pressure.

Trough water (flush water) - 17.5 pounds pressure.

Durability of canvas - 60 hours (average).

Benzene loss - 35.8 pounds per "sulphonation".

Sulphone - 25.4 pounds benzene per "sulphonation".

Soda press loss - 3.0 pounds per press (soda salt).

The soda-salt loss was unduly high and to overcome this there was suggested a feasible wash procedure as follows:

Feed the mother-liquor to an Oliver press on the second floor and run the same in the usual way but only give a scant wash. The cake removed at the scraper is then flushed to a tank below (with a heavy agitation fitted) and leached. The leach of about 50° Be'. is then filtered over another Oliver and given a heavy wash. The combined filtrates are then handled in the usual manner. It is said that the final combined weak soda liquor is of smaller volume and that the loss by this procedure is reduced from 150 to 30 pounds so the advantage is apparent. I partially verified this procedure in the laboratory in a rough way, but cannot absolutely vouch for it.

THE SODATION or CONVERSION of the CALCIUM SALT to the SODIUM SALT

A centrifugal pump delivered the Oliver filtrate to the sodation tubs. Here the calcium salt, remaining unconverted after the addition of the waste liquor in the lime tubs, was converted by the addition of soda ash. This soda ash amounted to 50-100 pounds and once in a great while as much as 300 pounds, depending upon the quality of the waste liquor. The use of the waste liquor made a saving of 85-95 percent of the soda ash that otherwise would have been used. Excess waste liquor over that used in this operation was turned to the sewer. 100 percent conversion would have been carried out with waste liquor if it had not been for the great difficulty of washing out excess sodium sulphate. As it was, the percentage was high - often excessively so.

The soda ash was added as the Oliver filtrate was pumped to the tub. By the time the tub was full, the ashed filtrate was ready to be filtered through the Shriver plate presses.

The operator made tests for "under" and "over" soda ash, and corrected for both. If "under soda" he added more soda ash and if "over soda" he added a little more Oliver filtrate. His test for "under soda" was a drop or two of soda ash solution added to a portion of the clear (filtered) liquor. A precipitate of calcium carbonate showed that there was still some calcium salt to be converted, so there was added more soda ash. His test for "over soda" was the addition of calcium chloride solution to a portion of the clear (filtered) liquor. A precipitate of calcium carbonate showed an excess of soda ash, so more Oliver filtrate was run in to use up this excess soda ash. When no precipitate was formed on the addition of either test reagent, the conversion was complete and correct.

$$Ca\,(C_6\,H_5\,SO_3)_2 + Na_2\,CO_3 \rightarrow 2\,C_6\,H_5\,SO_3\,Na + Ca\,CO_3$$

Excess

$$Na_2CO_3 + CaCl_2 \rightarrow 2NaCl + CaCO_3$$

The converted liquor was then pumped by a centrifugal pump to the Shriver plate presses above. The presses stood a pressure of 25-30 pounds before leaking. A "sulphonation" having been converted largely in the lime tubs and the resulting cake having been taken out at the Olivers little cake was formed in the sodation tubs. The result was, a Shriver would handle 6 or 7 "sulphonations" before it was necessary to dump it. Ordinarily the cake formed by a 100 percent soda ash conversion would fill a press. The press cakes were washed 'till the filtrate showed less than 0° Be'. at 75° C. As the cake was dumped, samples were taken from each plate and made into a representative sample for the control work.

The Shriver filtrate dropped by gravity to the weak liquor storage below on the first floor and the cake was flushed to

the sewer. This cake might have been utilized in the lime tubs, but, it being a comparatively small amount to bother with, was thrown away.

Canvas on the Shriver plates lasted a month or two and then many times had to be replaced only because the operator had punched a hole or two in same while cleaning. Many of the canvases wore through where they came in contact with the faces of the plates. The drip cocks had to be blown free of sulphone and carbonate with high pressure steam. To do this they were removed from the plates and screwed on to a nipple on a steam line and blown clear and then replaced on the plates. The feed lines to the presses were also steamed out at intervals.

EVAPORATION or CONCENTRATION of SODA LIQUOR

The hot 8.5° Be'. Shriver filtrate was drawn from the weak liquor storage tubs into the first effect of a double effect evaporator by suction. The liquor from the first effect was slowly drawn into the second effect. About 53 percent of the total water was taken out in the first effect and about 13° Be'. was reached. The remaining 47 percent of the water to be removed was taken out in the second effect and a liquor of about 24-25° Be'. was obtained. This 24-25° Be'. or wet salt at 90° C. had a consistency of thin syrup and was of a reddish amber color (due to waste liquor). If allowed to cool it became thick with the consistency of cheese curd. It had a greasy, slippery caustic-like feeling to the touch. When everything went smoothly the operation was continuous and as one tub was emptied another full tub was switched in its place. The 24-25° Be'.

liquor or wet soda salt was pumped, continuously to the fusion room storage. The soda salt pipe line in the fusion room had to be kept warm or the salt would freeze and clog. To prevent this a 1-inch steam line was laid alongside of the salt line and both lines were then wrapped with asbestos. By this provision the soda salt could be kept at 80° C.

The evaporating apparatus of the new plant consisted of two double effect Buflovak evaporators, with 1850 square feet of heating surface in each effect. The capacity of one double effect installation per hour was about 3700 gallons of water evaporated, and this was equivalent to about 35 tons of phenol per 24-hour day. A catch-all (or spray catcher) was fitted to the second effect of both installations to reclaim any salt carried over mechanically by the spray. A large wet vacuum pump (16"x22" x20") with a 48"x72" jet condenser maintained a 24" to 25" vacuum in the second effect. A

small condensate pump (8" x 10" x 12") helped maintain 15" of vacuum in the first effect and at the same time carried away the condensate from the steam chest of the second effect. A Worthington double acting steam pump (6" x 6" x 6") was used to pump the heavy concentrated salt from the second effect to the fusion room storage.

The old plant evaporating apparatus consisted of one installation identicalto those in the new plant and a Swenson double effect (basket type steam chest) installation of slightly smaller capacity.

In principle both evaporators work alike. The weak liquor was drawn into the first effect which maintains a vacuum of 15". From the first effect it was slowly but steadily sucked into the second effect. 13° Be'. was reached in the first effect. In the second it was taken to 24 to 25° Be'. The first effect was heated by exhaust steam, now and then boosted with live steam. The exhaust steam entered the chest at the rear, condensed,

gave up its heat, and the condensate flowed from the front of the chest by gravity to a trap. Water evaporated in the first effect was pulled to the chest of the second effect in the form of steam, where it condensed and gave up its latent heat to that cell. This condensate was pulled away by a small wet vacuum pump. This pump, with condensation of the steam from the first effect maintained the vacuum of 15". A large vacuum pump in conjunction with a large jet condenser pulled the vapor off of cell #2 and discharged it along with the condenser water to a large tank. A portion of this water went through a heater, and was then used on the Oliver presses. The remainder went to the plant spray-pond.

Both Swenson and Buflovak machines had their advantages. The former operated on 5 pounds of exhaust steam whereas the Buflovak required 8 to 10 pounds. The vertical tubes of the Swenson were more self cleaning than the horizontal tubes of the Buflovak and there was experienced no leaks with the basket chest of the Swenson where-

as the Buflovak tubes caused considerable trouble. The tubes of the Swenson basket, once expanded in the chest, never leaked. The Swenson bottom dropped out of place making the inside of the evaporator body open to the world, and the only means of entrance to the Buflovak cells was a small man-hole. The Worthington soda liquor pump served its purpose better than the magna ball valve pumpts of the Swenson apparatus. However, the Worthington pump was not standard equipment on the Buflovak. The two small single acting pumps furnished by Buflovak were absolutely no good for the heavy soda salt liquor. From the operators standpoint, the Buflovaks were easier machines to handle as the valves were more easily reached and fewer steps were required to operate same.

-EVAPORATOR REPORT-

Time	°Be' Tub	°Be' Cell #I	°Be' Cell #2	Inches-Vacuum Cell #I	Inches-Vacuum Cell #2	Steam-Pressure
8:30	6	I3.5	23.0	I5.0	24.5	8
9:30	9	I3.0	24.0	I5.0	24.5	8
I0:30	I0	I4.0	24.0	I5.0	24.0	8
II:30	I0	I4.0	24.0	I5.0	24.0	7.5
I2:30	I0	I9.0	24.0	I5.0	24.5	8
I:30	8	I3.0	23.0	I4.5	25.0	8
2:30	8	I3.0	24.0	I5.0	24.0	8
3:30	9	I3.0	24.0	I5.0	24.0	7.5
4:30	8	I2.0	24.0	I5.0	24.0	8
5:30	8	I3.0	24.0	I5.0	24.0	8
6:30	8	I3.0	24.0	I5.0	24.0	8

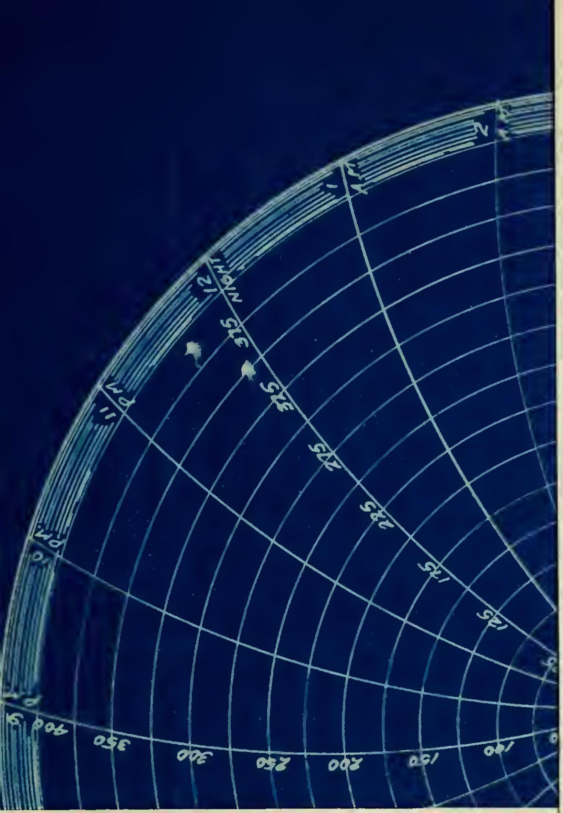
The average °Be' in the tubs was 8 at 65-70° C.

Swenson steam averaged about 5 pounds pressure.

THE FUSION of SODIUM BENZENE SULPHONATE with a CAUSTIC to PRODUCE SODIUM PHENATE (and SODIUM SULPHITE)

21-2200 pounds of 98° percent caustic (in lumps the size of a man's head) with 15-20 gallons of water were dropped into a fusion kettle and melted. The water hastened the melting. As soon as the caustic had become molten a motor-driven agitator was put in motion. Then, as the caustic mass reached a temperature of 275-80° C. the 24° Be'. or wet soda salt was started feeding slowly into the caustic from an overhead measuring tank. The total time to bring the cuastic to 275-80° C. was about 1.5 hours. The rate of feed of soda salt was judged by a template or guide line on the temperature recording chart. The soda salt was charged so that the pen point made an easy curve and approached 295-300° C. This temperature of 295-300° C. was maintained in the mass 'till the soda salt was all in the kettle. Six to 6.5 hours was the best charging time.

With 10-20 gallons of soda salt remaining in the measuring tank, the fire under the kettle was put out. After the salt was all in the kettle, the temperature mounted to 330-335° C. due to the heat of reaction. After the measuring tank had drained dry the charging line from the tank to the kettle was blown clear of salt with high pressure steam. The contents of the kettle were allowed to agitate and cook at this temperature for .5 of an hour. If the temperature went above 335° C. cold water was added to bring it down to 335° C. A good fusion at this stage looks like and was of the consistency of hot chocolate and had a specific gravity greater than 2. During the .5 hour cook an air-tight manhole cover was bolted in place and all valves except the vent valves were closed. The cook completed, the fusion was ready to be dissolved with hot water. Great volumes of steam issued from the kettle at the start of the melting and a small amount of the fusion was blown into the main. At the end of each shift this main

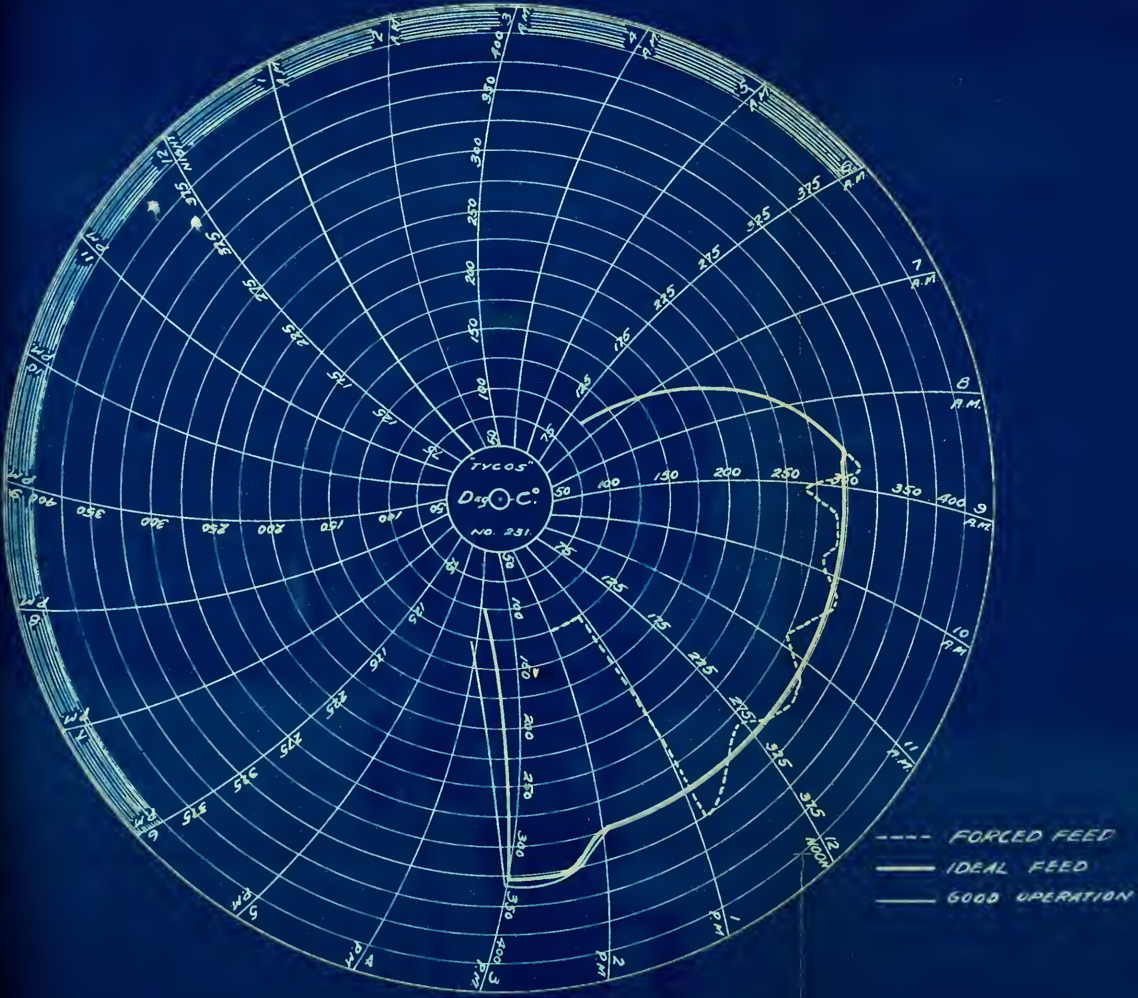


4845# 2150#

$C_6H_5.ONa + Na_2SO_3 + H_2O$

3122# 3388# 485#

(Ratio of 2.25 to 1 theoretical)



-FUSION-CHART-

R.D. Parrott '19

was flushed out into a circulating tank and thence the flushed material was pumped to a separator. The yield of this flushing about equaled that of a fusion. A half hour of this melting or dissolving more than doubled the volume of the fusion. This water was applied to the fusion on the surface, at the center, of the fusion mass 'till the temperature dropped to 125° C. The water then was shut off and the blow line opened, the vent line closed, 15 pounds of air applied at the surface of the fusion, and the fusion was blown to a separator for acidification. During the whole operation, except when the caustic was first charged, the agitator was in motion.

Theoretically soda salt and caustic should be fused in the ratio of 2.25 to 1. I believe, however, that the most efficient ratio, taking everything into consideration, is 1.5 to 1.

$$\underset{4845\#}{C_6H_5SO_3Na} + \underset{2150\#}{2\,NaOH} \rightarrow \underset{3122\#}{C_6H_5.ONa} + \underset{3388\#}{Na_2SO_3} + \underset{485\#}{H_2O}$$

(Ratio of 2.25 to 1 theoretical)

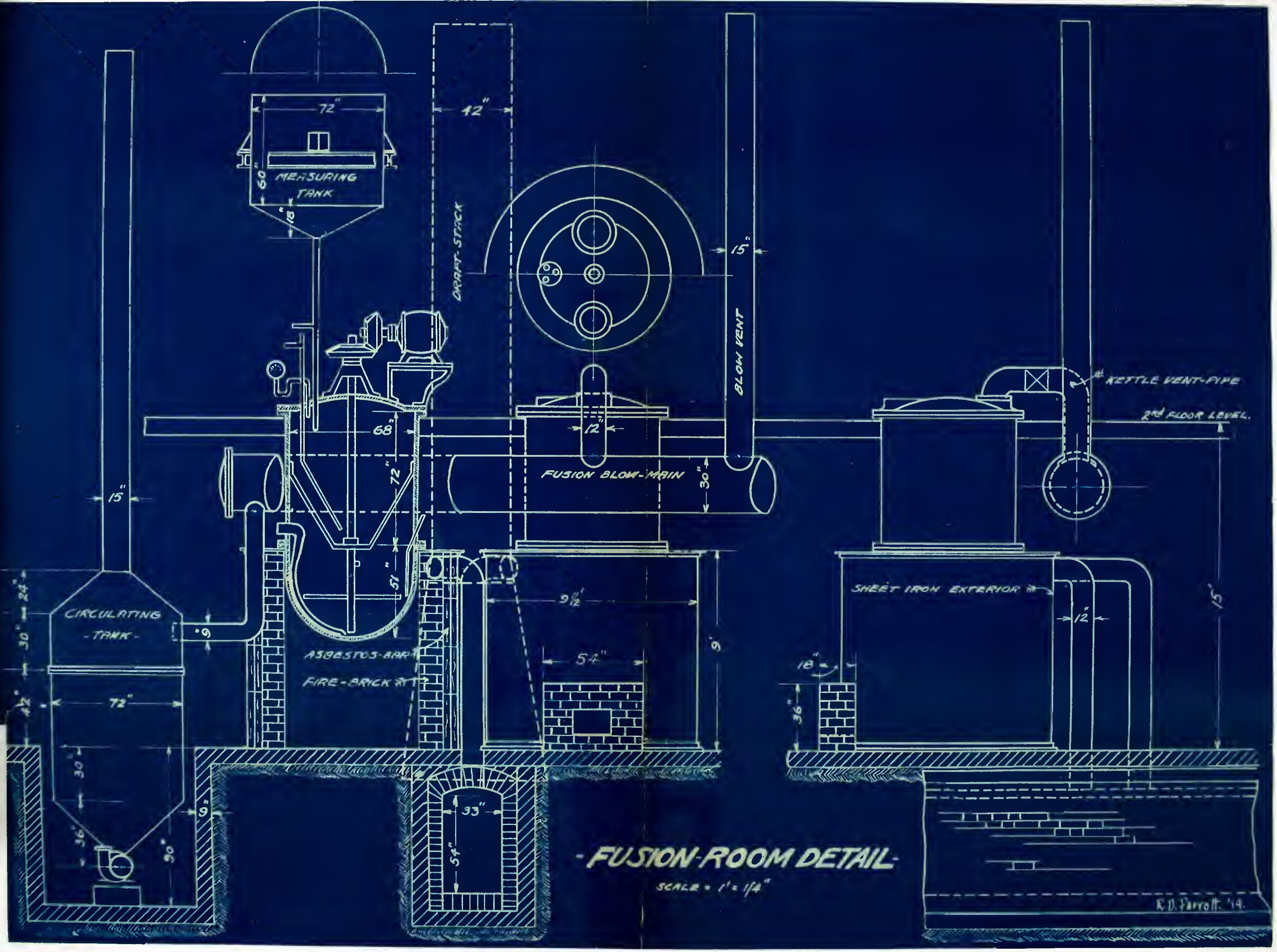
Finished fusions varied considerably, some being so thick that they could not be agitated, while others had the thinness of water. A few gave a crude that was white to straw color, but these were rate, the majority giving a crude that was reddish to brownish black. This dark color was largely due to charred soda salt and decomposition products. Some kettles were hotter than others and some kettles had better agitation than others. If an extra hot kettle and a poor agitation got coupled up together, plenty of charring and decomposition took place. A fusion that was charged too fast chilled on the surface, and thereby interrupted proper agitation. Two or three fusions reached 350-360° C. on the final cook due to low reading clocks. These fusions gave dark tarry crudes that were almost worthless.

After this impression had taken effect on all concerned, a goodly portion of my time was taken up in testing and correcting these recording clocks.

- THE FUSION ROOM -

A fusion took place in a large directly fired kettle supported by brick work which went to make up the fire hole. A cover on the kettle was fitted with water, air and steam connections, a manhole through which the fusions could be viewed, a stack vent, and a safety vent pipe which was fitted with a blank flange of permanite, a fiber asbestos-like material which would burst at about 30 pounds. A syphon leg was fitted in the kettle for removing the finished fusions. A small motor (5 horse) was mounted on the top of the kettle for driving the large agitator.

Crude oil fuel was burned at the tip of a steam atomizing spray nozzle. The flame was played in such a manner as to have it pass up around the kettle rather than directly against it. Ten-pound exhaust steam was used and the oil was fed at 30 pounds pressure. A temperature of 12-1300° C. was



- FUSION-ROOM DETAIL -

SCALE = 1' = 1/4"

72"
60"
MEASURING TANK
18"
42"
DRAFT-STACK
15"
BLOW VENT
KETTLE VENT-PIPE
2nd FLOOR LEVEL
68"
72"
51"
12"
FUSION BLOW-MAIN
30"
15"
24"
CIRCULATING - TANK -
30"
9"
42"
72"
30"
36"
30"
9"
ASBESTOS-BAR
FIRE-BRICK
9½'
9'
54"
33"
54"
SHEET IRON EXTERIOR
12"
18"
36"
15'
R.D. Parrott '14.

attained, and the average consumption of oil was about 200 gallons per fusion excluding the melting of the cuastic.

Above the fusion kettles were placed the measuring tanks 6 feet diameter by 6 feet high fitted with "telltale" floats. Above these were placed the storage tanks of two sizes, 7 feet diameter by 10 feet high, and 8 feet diameter by 8.5 feet high, eight of the former and ten of the latter.

- FUSION ROOM OPERATION -

There is only one way to operate, whether it be in the fusion room or not, and that is the right way. There being three shifts of workmen and all with the understanding that a maximum tonnage of phenol was the goal, there was a chance for jealousy and competition. Each shift fought and tried to turn out more phenol than the others. This was true of every department and especially true of the "sulphonation" and fusion departments. This (by no means little) element of jealousy was very apparent in the fusion room. Short-time fusions, thick fusions, black fusions, and in the end inefficient fussions were the result. For many months it was an unheard of thing to have a single kettle charged twice on the same shift. But at last when the rush was on, a very hot fire (which burned out kettles) helped hasten the charging of the soda salt. The hastened charging made for poor agitation due to chilling. The chilling

made thick fusions because too little time was allowed for chemical reaction. The thickening made for black fusions and in the end a small yield.

By a good fusion, I mean one that was not fired too fast to burn, and one in which the soda-salt feed was steady. The irregular curve tells the story of a rush fusion. The bumps show where the feed was slackened to allow the temperature of the mass to rise rapidly to a temperature greater than was actually needed. Once thie temperature was reached, soda salt was run in at an enormous rate until the pen point struck "some place around" 300° C. more or less. This procedure emptied the measuring tanks in a shorter time than was regularly taken and put many a finished fusion down on a shift report long before it should have been there. When it was possible (and that was often) as much as 6 to 18 inches or 400-1200 pounds of soda salt were allowed to remain in the measuring tank thus "short weighing" a fusion. This

meant waste of money and time. To cover up this thievery, the measuring tank would be filled up immediately, upon the pretense of being in a hurry to make up a charge of soda salt for another fusion. This sort of business went on for many weeks and during this time it did not surprise me to run on to a 2-inch yield of phenol instead of a normal yield of 4 or 5 inches. These 2-inch yields never got into reports for it was easy to juggle a 2 and a 5-inch yield to make two 3.5-inch yields. After considerable (undue) agitation on my part, strict watch was put over this matter.

The efficiency of the fusion room as a whole averaged about 75 percent. A rush fusion would go about 60-70 percent and a good fusion 80-90 percent, depending upon the many conditions. Some individual fusions ran higher.

Soda Salt varied from day to day in specific gravity as well as in purity. For this reason, especially from the standpoint of specific gravity or soda salt content, a

constant single volume measure could not be used for all fusions. So a chart was made reading pounds, temperature, beaume', and "inches in measuring tank". For a given charge of caustic, the operator figured from his ratio of soda salt to caustic, the required amount of soda salt needed in pounds. He then ascertained the temperature and beaume' of the wet salt. Having these necessary figures he read off the "inches of soda salt in the measuring tank" required to make up his figured poundage, after which he allowed the correct number of inches of wet salt to run into the measuring tank from his storage. Instead of going way up above the storage tanks to get the temperature and beaume' he allowed about half a charge to run into the measuring tank and then took his measurements there.

The following is a copy of the anonymous report concerning the charging chart:

"Four content determinations were made with solutions at 95° C. with the follow-

ing results:

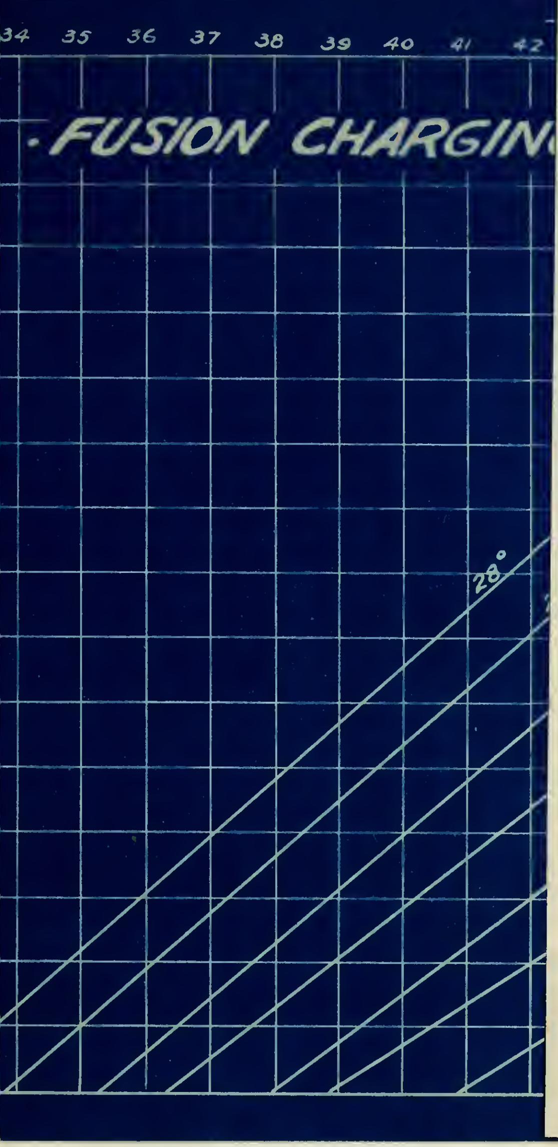
Be'. Reading	Grams / 250 cc	Pounds / Gallon
13	78	2.60
20	114	3.80
23	131	4.37
24	141	4.70

With these four points of "Be'." and "pounds" a curve was constructed from which the pounds corresponding to 18°, 19°, 22°, 25°, and 26°, 27°, and 28° Be'. were estimated per gallon. A charging chart was then made. (See Chart).

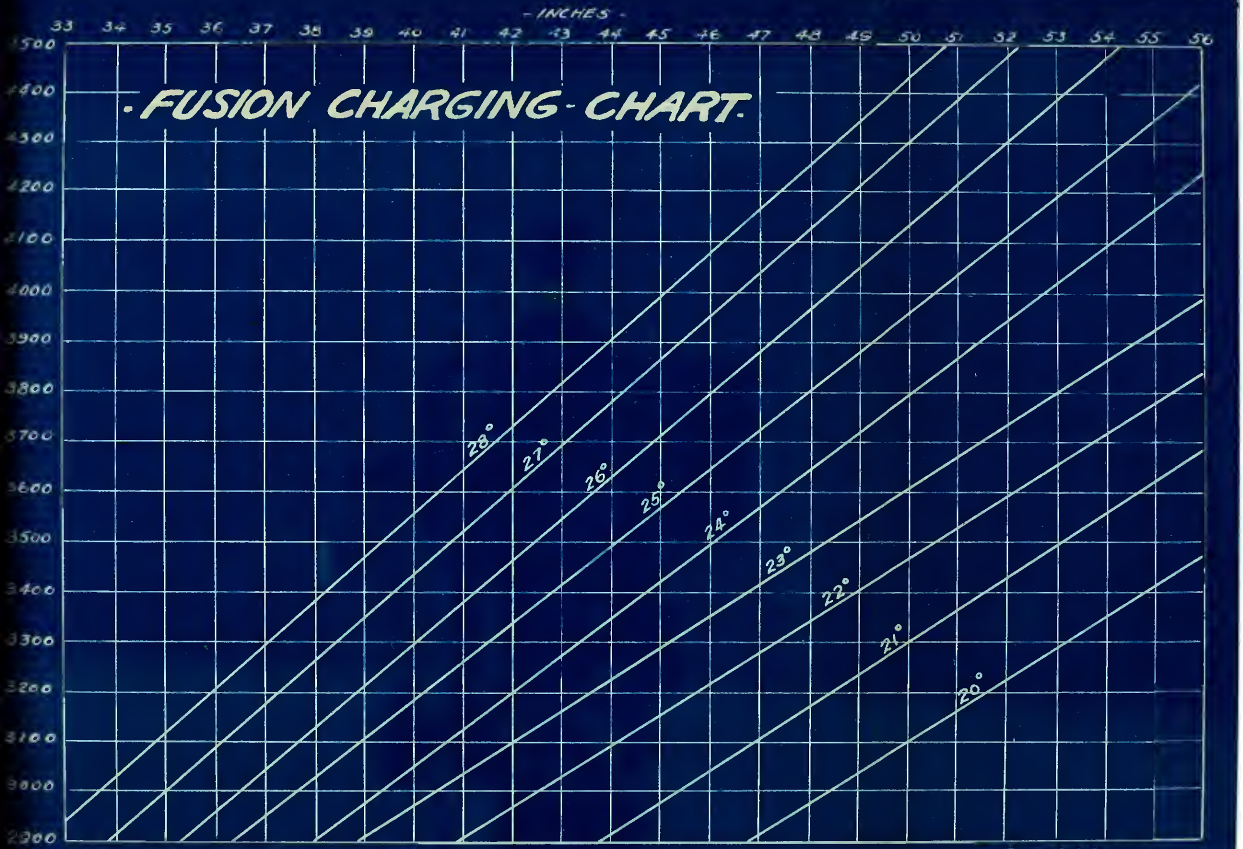
In experimenting with various concentrations of soda salt and varying temperatures, it was found that the beaume' reading varied 1° Be'. (approximately) for each 10° change in temperature, i.e., a solution of soda salt whose Be'. was 23° at 95° C., was 24° Be'. at 85° C.

From the charging chart the following figures were obtained for 3500 pounds of salt:

39.4 inches - 28 Be'.
40.8 " - 27 "
42.5 " - 26 "
44.1 " - 25 "
46.1 " - 24 "
48.2 inches - 23 Be'.
50.5 " - 22 "
53.0 " - 21 "
56.3 " - 20 "



calculations of inches (in charging tank) for different gravities are wrong (as 46.1 = 24° Be'., etc.). These calculations may have



·FUSION CHARGING·CHART·

R. D. Parrott '19.

The average difference in inches per 1° Be'. is 2.1 inches from 3500 pounds of salt at 95° C. Therefore the average difference in inches per 10° of temperature is 2.1 inches or approximately one inch for 5° difference in temperature.

Therefore since the kettles are charged with 3500-3600 pounds of soda salt solution, one inch of charge should be added to the number read on the chart calibrated for 95° C. for every 5° C. below 95° C.

Hence for a temperature of -

90° C. add 1 inch of liquor
85° C. " 2 inches " "
80° C. " 3 " " "
75° C. " 4 " " "
70° C. " 5 " " "

Then for a charge of 28° Be'. liquor of 3500 pounds at 75° C., we would add 39.4 and 4 inches which is 43.4 inches of liquor.

It is my opinion that the above figures are in error. Even the mathematical calculations of inches (in charging tank) for different gravities are wrong (as 46.1 = 24° Be'., etc.). These calculations may have

been correct for a certain tank, but not for the existing tanks of 17.6 gallons per inch. No allowance was made for impurity of salt in a first chart. A second revised chart allowed for five percent impure solids, and this might better have been ten percent as one can see from the following fusion table. It is this second chart that I am reproducing, using the figures as quoted in the above report. This chart although incorrect served the purpose and was to all practical purposes just as good as one 100 percent correct. Correct or incorrect the chart will give the reader the idea.

Figures that may be nearer correct (although I cannot vouch for them) are as follows:

°Be'.-95°C.	lbs./Gallon	°Be'.-95C.	lbs./Gal.
5	.70	17	3.05
6	.88	18	3.26
7	1.06	19	3.48
8	1.24	20	3.55
9	1.43	21	3.75
10	1.62	22	3.90
11	1.82	23	4.05
12	2.01	24	4.25
13	2.21	25	4.45
14	2.42	26	4.60
15	2.63	27	4.75
16	2.84	28	4.92

(See chapter on "Methods of Analysis" for a table of specific gravities at 23° C.)

-FUSION' RECORD-

Number Charged 51 Number Dipped 55 Date I2-I-'I7..

Kettle	Fusion No.	Lbs. Caustic.	Lbs. Soda Salt	T°	Be°	In"	Time Start	Time All In	Time Melt	Time Syphon	Finish Syphon	Total Time*	Nature
I	2I50	2094	3664	75	23	54	3:45A	I0:30A	I0:55A	II:20A	II:45A	6:45	Thin
I3	2I5I	2229	3900	80	25	52	4:00A	I2:05P	I2:30P	I2:45P	I:I0P	7:05	"
8	2I52	2229	3900	80	24	54	6:20A	II:45A	I2:I5P	I2:50P	I:20P	5:25	"
9	2I53	2I77	3809	80	24	53	8:00A	I:55P	9:35P	I:50P	2:25P	5:55	"
I9	2I54	2229	3900	70	24	57	9:20A	4:35P	5:05P	5:35P	6:I5P	7:I5	"
22	2I55	2I24	3747	75	26	50	I2:I5P	5:I5P	6:00P	6:30P	7:20P	5:00	"
2I	2I56	2I57	3827	75	25	53	I:30P	7:00P	7:40P	8:30P	9:35P	5:30	2
I6	2I57	2268	3969	75	24	57	7:00P	II:55P	I2:35P	I:00A	I:I5A	4:55	"
I7	2I58	2290	4007	75	25	54	II:I5P	4:30A	5:I5A	5:45A	6:30A	5:I5	"
II	2I59	2296	40I8	70	25	55	I0:50P	3:50A	4:35A	5:20A	5:95A	5:00	"
24	2I60	230I	4026	75	25	55	I2:30A	6:I0A	6:50A	7:I5A	7:50A	5:40	"

* Exclusive of cook.

- SOME DIFFICULTIES of the FUSION ROOM -

When the plant was new considerable trouble was experienced in the fusion room. Fusions were moved from the kettles with the aid of steam syphons. At the time I first went with the plant, fusions were being syphoned directly to a trough and a connected circulating tank located in a pit below the kettles. From this circulating tank the fusions were pumped to the separators for acidification. This circulating tank was made ready for a fusion by dropping into it 150-200 gallons of water and circulating it from "tank to trough" and then flowing it back to the tank by gravity, etc. The object of this circulation was to keep the fusion material from freezing and clogging the path. Much trouble was had with the syphons (one for each kettle), trough, tank, and the centrifugal circulating pump. The syphons were short-lived, always being eaten away by the hot fusion (and excess.caustic). The trough

and tank developed leaks, and the pump required constant packing. From this installation the next change was to put the circulating tank into an adjoining room where workmen could get at the pumps more easily. In this tank the circulation was out the bottom and in the top, and instead of a trough a 5-inch pipe was used to which all the kettles were connected by short leads. The syphons were placed at the kettle end of the leads and their function was to suck the fusion from the kettle and force it to the circulating tank. This was not satisfactory as the fusion solidified in the main before it reached the circulating tank and as a result the line had to be torn down and steamed out. The syphons were then changed from the position next the kettle to one directly over the circulating tank, and instead of having one for each kettle one served for about eight kettles. Leaks in the lines then bothered - but even so, this arrangement worked fairly well. "Freeze-ups" still

occurred often and especially at shift changes. It was customary to flush out all used lines with hot water to remove any solid matter. The next improvement was to do away with the syphons (largely) and blow the fusions to the circulating tank. The circulating tanks still gave trouble so the final step was to blow the fusions directly to the separators.

At the same time the trough and circulating tank were in use, and up to a short time after the fusions were blown with air, the fusions were melted by applying water through the syphons. Water applied like this at the bottom and near the surface of the kettle cracked the kettle. At this time a very fair life for a kettle was one month. Some kettles lasted only two weeks. Not only was this a costly and disadvantageous operation but it was a dangerous one too. When water was applied through this syphon, steam issued forth from the top of the kettle in great clouds and often fusion matter spattered and blew to the roof. I have seen whole

fusions expelled from the kettle with this procedure. It was a thrilling proposition for an on-looker to be any place near a fusion that was being melted up in this manner, let alone the position the melter took at the end of a 10-foot valve-extension rod. The later method of melting from the top lengthened the life of a kettle from 1 to 5 months and eliminated the unnecessary delays of 24-48 hours required to take out the old kettle and put a new one in its place. With the new way of melting, the ferocious steaming and spattering of old was subdued to that of the meekness of a lamb and the fusion room became parlor-like in comparison.

At the time I went to the plant, some trouble was being had with the stacks, both to the kettles and fire holes.

The stacks to the kettles had "hangs" form in them which partially clogged them. This made for bad operation on the fusion floor. Funnel-like sections helped to eliminate this trouble. Then at the suggestion of a laborer

(a Pole who could not talk English) sprays were put in the stacks. Together these aids kept the stacks clear.

During this same period goodly quantities of fusion matter were blown to the roof during the melting operations. If there was no wind (and this was seldom) the matter fell on the roof and was recovered, but if there was a wind it scattered broadcast and was lost. Often times, I have seen it thick enough upon the ground to make a print of a show in it like in snow. To eliminate this loss to the roof, very efficient baffle-caps were placed on the tops of the stacks. These had a tendency to make the stacks refluxing.

The fire-hole stacks became clogged once in a while from poor combustion, etc. When they could not be cleaned by dropping a brick down through them from the roof, they had to be torn down and cleaned by hand. One could often forecast a clogged stack by the way the kettle heated. A kettle that was unusually difficult to heat generally told the story.

The caustic soda was handled in sort of a crude way but even at that I believe it was the best. The large drums of caustic containing 675 pounds (net weight) were hammered such that the solid mass was cracked and broken up and the sheet iron drum remained intact. This drum was then rolled in on the fusion floor to a position in front of a kettle. A caustic hand then ripped off the drum or sheet iron shell with the aid of a shovel, whence the broken and cracked caustic fell apart into chunks the size of a man's head. These chunks were then thrown or shoveled into the kettle by hand. A year back the drums were hammered with sledges by hand, but later a very efficient trip hammer-like affair did the work.

Somebody had the brilliant idea that crushed caustic would melt in less time than the lump caustic and at the same time be easier to handle. The result was a great big "white elephant" of a crusher building and a crusher in it. The drummed material was freed from the drum and then broken up into pieces

small enough to feed to the crusher. The crusher was started and there was so much dust made that the operator had to leave the building. The resulting product was dropped to a small car and then pushed to the kettle to be charged. The attempt was an utter failure because it took twice as long to melt this material as it did lump caustic. Also the crushing operation and the handling were made difficult by the great quantities of dust.

- EXPERIMENTAL FUSIONS -

About 40 fusions, extending over a period of 7 or 8 weeks, were followed through from beginning to end. Measurements and samples were taken of all raw materials and finished products. A complete analysis was made on the soda salt and the phenol content was determined in the fusion melt, crude phenol and waste liquor. The caustic was sampled by the batch and not by the individual can. It was very pure, running around 98-99 percent.

The caustic charge was noted when it was put into the kettle, and the soda salt was accurately measured into a calibrated measuring tank and the specific gravity and temperature taken. Fusion melt and waste liquor were measured in a calibrated separating tank. The crude phenol was measured in the crude storage tanks.

Several graphs were made and a brief and somewhat disconnected discussion was drawn up on the same. It was found difficult to

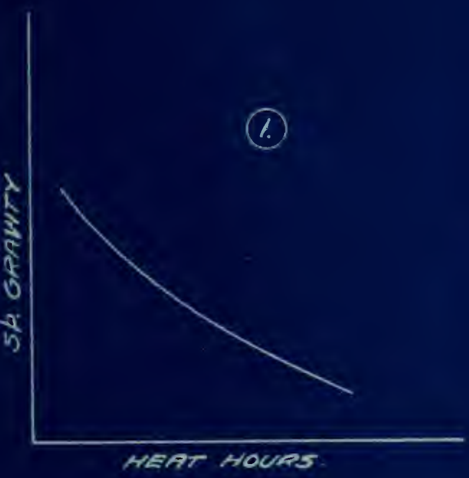
draw any hard and fast conclusions due to the many variables involved, a few of which are: Ratio of soda salt to caustic, impurities, fire, fast and slow kettles, duration of cook and agitation, etc., etc. One constant is the temperature (of the caustic bath) at which the soda salt is charged - namely 300° C.

I have assumed heat energy varied directly as the duration of the fusion operation; that specific heat of solids (soda salt and $Na_2 SO_4$ etc.) is .3 B. T. U. which is theoretical; that B. T. U. multiplied by hours equals heat hours -

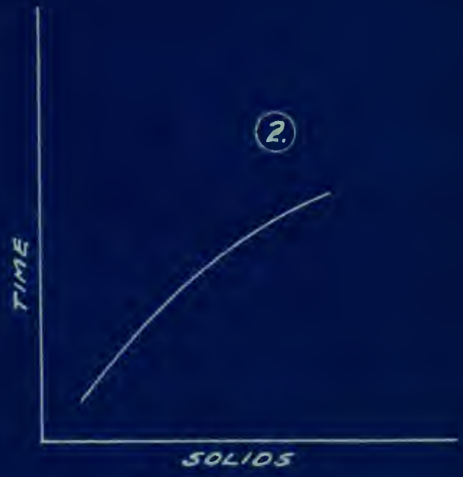
- On the Graphs -

1 lb. H_2O from 80° C. to Steam = (approx.) 1000 B.T.U. 1 lb. Solids from 80° C. to 300° C. = (approx.) 120 B.T.U. Heat hours = (B.T.U. required to take the water from 80° C. to steam) + (B.T.U. required to raise the salts or solids in the charge from 80° C. to 300° C.)

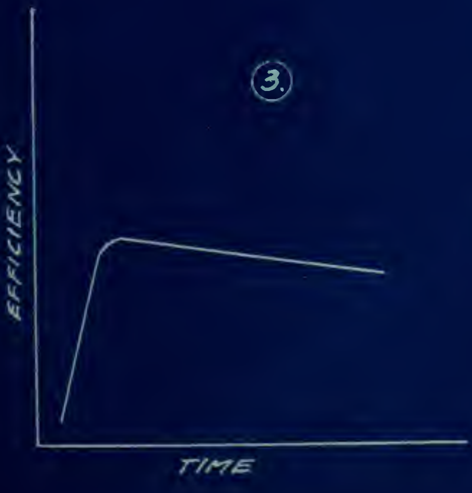
①



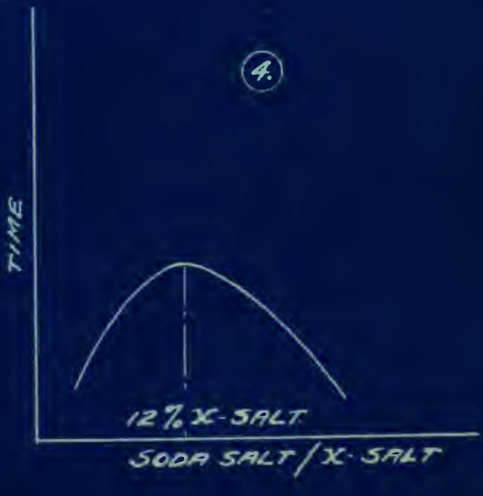
②



③



④



R.D. Parrott '19.

Time equals that time required to charge a fusion (exclusive of the cook).

Soda salt to caustic ratio is the actual ratio of pure soda salt charged, to the caustic used in the fusion.

Efficiency is based on the soda salt in the charge and phenol content of the melt.

"X" salts mean pounds of foreign solids ($Na_2 SO_4$ - $Na_2 CO_3$ - traces of calcium salts).

The time of charging a fusion (chart 1) increases as the specific gravity of the soda salt decreases, or as the ratio of water solids increases (chart 2) and as the charge increases. This is as one would expect.

Duration of charge (chart 4) increases to a maximum as the "X" salts decrease from a maximum to about 12 percent of the total solids, and then decreases as the "X" salts approach a minimum. This may mean that a soda salt with a 12 percent impurity absorbs more heat or is capable of greater reaction and

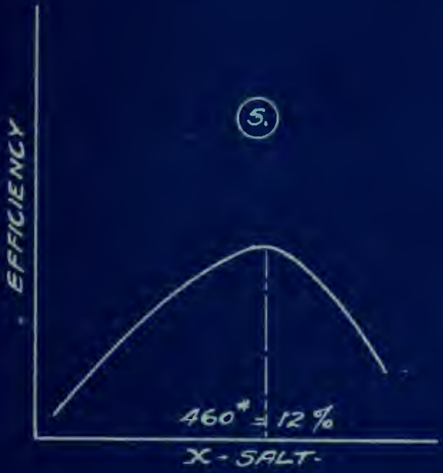
requires a greater quantity of heat, than otherwise, to start this reaction.

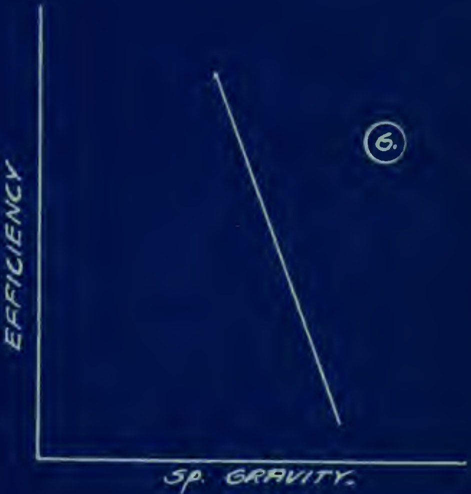
The efficiency (chart 3) increases rapidly for a comparatively short time at the start and then decreases as the time increases. This may be due to the great excess of caustic soda which is present at the start (mass action). As the time increases this excess of caustic decreases and the soda salt and "X" salts increase.

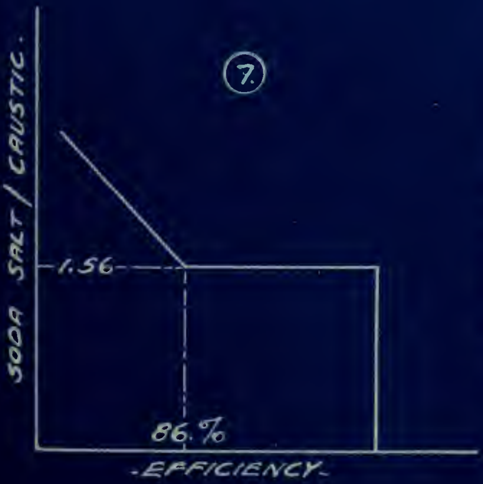
Diphenate and decomposition products, along with the wastage of soda salt, by charring, lower the efficiency.

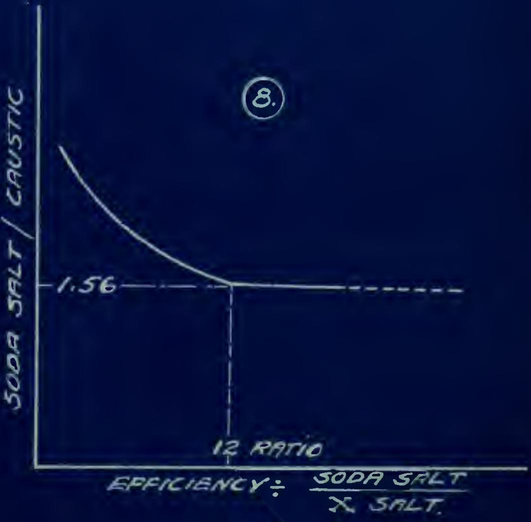
The efficiency of a fusion (chart 5) approaches a maximum as the "X" salts approach 12 percent of the total solids and then decreases as the "X" salts increase further. Considering 3840 pounds as an average total solid content of a charge, 12 percent of "X" salts would be about 400 pounds.

The efficiency increases (chart 7) as the ratio of soda salt to caustic decreases to a point representing 1.56. A









R. D. Parrott '19

lower ratio means a waste in caustic as the curve tends to follow a straight line parallel with the efficiency axis.

The efficiency increases (chart 8) and approaches 100 percent as the soda salt caustic ratio approaches 1.56 and the soda salt purity approaches 88 percent.

Theoretically an exothermic reaction is furthered when cold is applied or when the heat of reaction is removed from the sphere of reaction. "Soda salt plus caustic to the formation of phenate" is an exothermic reaction, and a condition of the reaction is a molten-bath. Theoretically, all heat over that necessary to maintain the bath molten should be removed.

During the period of charging, the heat required to vaporize the water and to raise the "X" salts in the charge satisfies the above. I believe it is the evaporation of the water that removes the bulk of the heat of reaction and makes a wet fusion more efficient than a dry fusion. When the charge is all in, the fire under the kettle should be removed.

Ideally the fire chamber should be cooled immediately to a temperature just great enough to maintain the bath molten. The "X" salts such as Na_2SO_4, Na_2CO_3 and Na_2S are infusible at 325° C. so they must exist as a suspension. In this condition these impurities may act as a carrier to remove the heat of reaction, or perhaps may act as positive catalytic agent.

Efficiency, then, approaches a maximum when the impurities (Na_2SO_4, etc.) approach 12 percent of the total solids in the charge; the soda salt to caustic approaches 1.56, and the concentration of the soda salt approaches a maximum rather than a minimum. Six or seven hours with the proper fire should be about the correct time rather than three or four hours.

-FUSION TABLE-

No.	Pounds of Caustic	Ratio Soda-Salt Caustic	Ratio Soda-Salt "X" Salts	Ratio Water T.Solids	Ratio Eff. Soda Salt "X" Salts	Hours to Charge Soda Salt	Heat-Hours	Fusion Melt in Gallons	Waste-Liquor Gallons	Phenol per Gallon Fusion Melt.
I	2025	I.80	I5.30	I.40	5.52	5.25	3I.60	I540	I549	I28.0
2	2I50	I.38	I4.40	I.94	6.00	6.I8	37.20	I45I	I549	III.0
3	2025	I.56	5.90	I.34	I5.30	5.00	27.00	II43	I332	I6I.2
4	2025	I.I4	2.93	I.56	30.05	7.00	36.I2	I072	----	I20.0
5	2025	I.5I	7.20	I.49	I2.75	6.42	36.20	I505	I556	II6.4
6	2I53	I.90	I2.50	I.27	6.I2	5.75	34.40	I574	I593	I24.6
7	2025	I.5I	5.80	I.63	I4.30	7.66	48.20	I645	I743	II2.0
8	2I09	I.30	I0.75	I.36	8.3I	7.00	40.20	I750	I8I8	II5.7
9	2025	I.60	I0.I0	I.45	9.07	6.08	34.20	I630	I695	II4.0
I0	2I95	I.46	8.50	I.38	II.60	5.60	27.60	I360	I300	I46.4
II	2025	I.28	4.20	I.5I	20.08	5.66	29.70	I435	I549	99.6
I2	2025	I.60	8.80	I.50	9.50	5.75	5I.60	I773	I860	96.0
I3	2025	I.87	I4.I5	I.23	5.04	3.75	20.50	I574	I593	II0.0
I4	2229	I.57	6.90	I.55	I2.65	8.25	55.30	I667	I800	II4.7
I5	225I	I.73	II.65	I.47	7.44	I0.66	7I.40	I468	I460	I44.0

-FUSION TABLE- cont'd.

No.	Pounds of Caustic	Ratio Soda-Salt / Caustic	Ratio Soda-Salt / "X" Salts	Ratio Water / T.Solids	Ratio Eff. Soda Salt / "X" Salts	Hours to Charge Soda Salt	Heat Hours	Fusion Melt in Gallons	Waste Liquor Gallons	Phenol per Gallon Fusion Melt.
I6	2025	I.54	9.25	I.52	I0.22	5.00	28.45	I467	I433	I25.6
I7	2025	I.64	8.I5	I.43	I2.I5	8.00	47.68	I334	I342	I60.0
I8	2229	I.67	7.94	I.42	II.80	6.50	42.25	I628	I695	I35.0
I9	2I60	I.74	II.45	I.33	8.00	6.37	38.70	I293	I300	I70.0
20	2264	I.75	8.55	I.3I	I0.50	5.50	35.00	I260	I270	I78.0
2I	2025	I.74	8.80	I.35	I0.30	7.50	43.25	II43	II08	I75.0
22	2025	I.84	I3.00	I.30	8.57	6.50	36.90	I450	I487	I58.0
23	2025	I.8I	II.I0	I.I2	7.24	4.42	2I.85	I377	I300	I34.0
24	2025	I.74	9.50	I.37	8.60	8.00	46.40	I5I0	I565	II7.0
25	2025	I.68	9.50	I.40	I0.22	6.84	39.40	II30	II80	I84.0
26	2025	I.43	9.32	I.4I	9.75	6.25	30.70	I3I9	I390	I24.6
27	2229	I.67	II.II	I.53	8.27	7.80	52.50	I360	I390	I57.8
28	2025	I.7I	6.55	I.44	I4.90	6.00	37.38	I393	I390	I49.0
29	2025	I.65	5.84	I.42	I4.40	6.00	35.20	I230	I390	I40.4
30	2025	I.94	6.90	I.40	II.55	7.00	47.88	I650	I750	II8.0

-FUSION TABLE- cont'd.

No.	Pounds of Caustic	Ratio Soda-Salt / Caustic	Ratio Soda-Salt / "X" Salts	Ratio Water / T.Salts	Ratio Eff. Soda Salt / "X" Salts	Hours to Charge Soda Salt	Heat-Hours	Fusion Melt in Gallons	Waste Liquor Gallons	Phenol per Gallon Fusion Melt.
3I	2025	I.65	8.00	I.40	I0.00	7.00	39.90	I220	I300	I37.0
32	2269	I.70	I2.60	I.39	7.I8	4.50	27.63	I392	I450	I54.0
33	2025	I.82	I4.40	I.33	6.50	5.00	30.05	I078	II30	200.0
34	2025	I.76	II.50	I.33	7.28	8.00	46.80	III8	II60	I67.0
35	2269	I.70	9.66	I.34	9.20	4.50	27.36	I360	I400	I54.0
36	2269	I.73	II.70	I.29	7.70	5.00	30.00	I305	I360	I70.0
37	2025	I.56	7.87	I.37	I2.00	5.00	26.50	I478	I700	I27.0
38	2269	I.63	II.50	I.27	8.I5	4.00	22.84	I475	I500	I48.0
39	2025	I.72	9.95	I.39	8.40	5.00	28.85	I375	I300	I43.0

-FUSION TABLE-

No.	Percent Effic-iency	Sp.Gr. Liquor	°C. of Liquor	Liquor-Vol. of Gallons	Pounds Liquor	Pounds Total Solids	Pounds Water	Pounds Soda-Salt	Lbs. of"X" Salts.
I	84.80	I.I69	85	976.8	9520	3970	5550	37I7	243
2	86.40	I.I32	85	985.6	9293	3I65	6I28	2974	I9I
3	9I.30	I.I88	80	877.6	8685	3705	4980	3I73	532
4	89.30	I.I94	80	792.0	7877	3080	4797	2298	782
5	9I.70	I.I84	85	880.0	8680	3480	5200	3055	425
6	76.50	I.I7I	85	I029.0	I0050	4420	5630	4092	328
7	97.45	I.I84	82	959.0	9428	3590	5838	3064	526
8	89.30	I.I80	85	932.8	9I70	3890	5290	3550	330
9	9I.58	I.I70	89	897.6	8752	3562	5I90	324I	32I
I0	98.87	I.2I2	80	870.2	8786	3696	5090	32I7	379
II	87.60	I.I90	80	8I8.4	8086	3226	4860	2604	622
I2	83.30	I.I94	75	9I5.2	9I06	3636	5460	3264	372
I3	73.I0	I.I86	85	9I5.2	9042	4052	4990	3787	267
I4	87.25	I.I73	90	I047.2	I023I	40II	6220	3503	508
I5	86.60	I.I80	80	I065.0	I0465	4235	6230	3905	335
I6	94.30	I.I68	85	897.5	8740	3460	5280	3I22	338

-FUSION TABLE- cont'd.

No.	Percent Efficiency	Sp.Gr. Liquor	°C. of Liquor	Liquor-Vol. of Gallons	Pounds Liquor	Pounds Total Solids	Pounds Water	Pounds Soda-Salt	Lbs. of "X" Salts.
I7	99.00	I.I82	95	950.0	9350	3850	5500	3430	420
I8	94.00	I.I88	75	I030.0	I0200	4200	6000	3730	407
I9	9I.50	I.I90	85	967.5	9600	4I20	5480	3760	360
20	90.00	I.I85	90	I038.0	I0260	4430	5830	3965	465
2I	90.75	I.I87	80	935.0	9225	3925	5200	3525	400
22	98.50	I.I85	90	932.8	9200	4000	5200	37I5	285
23	80.20	I.I80	86	862.4	8470	4000	4470	3670	330
24	80II5	I.I88	85	932.8	9230	3890	5340	3520	370
25	97.40	I.I85	85	9I6.2	9050	3770	5280	34I0	360
26	90.75	I.I87	70	792.0	7732	3200	4532	2890	3I0
27	9I.75	I.I79	70	I038.4	I0300	4060	6230	3735	335
28	97.50	I.I96	88	976.8	9750	4000	5750	3470	530
29	84.30	I.I94	70	932.8	9280	3830	5450	3270	560
30	79.80	I.I95	75	I083.4	I0800	4500	6300	3930	570
3I	80.00	I.I83	85	9I5.2	90I5	3754	5258	3340	4I7
32	90.50	I.I77	88	985.6	9750	4085	5665	3785	300

-FUSION TABLE- cont'd.

No.	Percent Effic-iency	Sp.Gr. Liquor	°C. of Liquor	Liquor Vol. of Gallons	Pounds Liquor	Pounds Total Solids	Pounds Water	Pounds Soda Salt	Lbs. of"X" Salts.
33	93.50	I.I80	85	950.4	9350	40I3	5337	3690	323
34	83.70	I.I90	80	950.4	9425	4048	5377	3565	483
35	88.40	I.I78	77	994.4	9760	4I77	5583	3785	392
36	90.50	I.I90	90	985.6	9770	4254	5496	3920	334
37	94.30	I.I80	90	864.2	8420	3573	4897	3I70	403
38	93.70	I.2I0	70	924.0	9330	4I03	5227	3720	383
39	84.20	I.200	85	9I5.2	9I50	3830	5320	3480	350

-FUSION TABLE- ANALYSIS of SODA SALT (wet basis)

No.	Percent H_2O	Percent Soda Salt	Percent Na_2SO_4	Percent Na_2CO_3	Percent CaO
I	58.22	39.04	2.07	0.67	
2	65.95	32.00	I.28	0.77	
3	57.I3	36.53	5.49	0.85	
4	60.80	29.I8	9.4I	0.6I	
5	59.88	34.93	4.52	0.69	
6	55.99	40.77	2.44	0.80	
7	6I.09	32.47	5.74	0.80	
8	57.74	38.69	3.I6	0.4I	
9	59.39	37.03	3.I8	0.39	
I0	57.92	36.62	4.6I	0.85	
II	60.I2	32.I9	6.27	0.42	
I2	60.I5	35.85	3.65	0.35	
I3	55.I0	5I.88	2.46	0.49	0.II
I4	60.82	34.24	4.47	0.47	
I5	59.65	37.3I	2.53	0.5I	
I6	60.43	35.74	3.37	0.46	
I7	58.67	36.7I	4.00	0.62	

-FUSION TABLE- ANALYSIS of SODA SALT (wet basis) cont'd.

No.	Percent H_2O	percent Soda Salt	percent Na_2SO_4	percent Na_2CO_3	percent CaO
I8	58.86	36.78	3.I5	I.2I	
I9	57.I3	39.I4	2.89	0.84	
20	57.65	38.64	2.8I	0.90	
2I	57:26	38.I7	2.33	I.24	
22	56.55	40.38	2.26	0.8I	
23	52.90	43.25	3.I0	0:75	
24	57.80	38.06	3.43	0.7I	
25	58.33	37.70	3.29	0.68	
26	58:64	37.40	3.47	0.49	Trace
27	60.05	36.3I	3.05	0.59	
28	58.92	35.59	4.69	0.80	
29	58.83	35.22	5.08	0.87	
30	58.3I	36.37	4.50	0.82	
3I	58.33	37.05	3.76	0.86	
32	58.I0	38.85	2.48	0.57	
33	57.08	39.50	2.7I	0.7I	
34	57.05	37.85	3.29	0.8I	
35	57.20	38.85	3.I2	0.83	Trace

-FUSION TABLE- ANALYSIS of SODA SALT (wet basis) cont'd.

No.	Percent H_2O	Percent Soda Salt	Percent $Na_2 SO_4$	Percent $Na_2 CO_3$	Percent CaO
36	56.25	40.IO	2.90	0.74	Trace
37	57.82	37.43	4.08	0.67	
38	56.02	39.82	3.47	0.69	
39	58.IO	38.06	2.99	0.85	

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

-FUSION TABLE - ANALYSIS of SODA SALT (dry basis)-

No.	Percent $Na_2 SO_4$	Percent $Na_2 CO_3$	Percent Soda Salt
I	4.96	I.36	93.68
2	3.77	2.26	93.97
3	I2.82	I.99	85.I9
4	24.0I	I.55	74.44
5	I0.99	I.62	87.39
6	5.54	I.82	92.64
7	I4.76	I.55	83.69
8	7.02	0.98	92.00
9	7.84	0.97	9I.I9
I0	I0.96	2.04	87.00
II	I5.73	I.06	83.2I
I2	9.I7	0.87	89.96
I3	5.45	I.II	93.33
I4	II.4I	I.20	87.39
I5	6.25	I.25	92.49
I6	8.59	I.I5	9I.26
I7	9.67	I.49	88.84
I8	8.53	2.06	89.4I

- FUSION TABLE - ANALYSIS of SODA SALT (dry basis) cont'd.

No.	Percent $Na_2\ SO_4$	Percent $Na_2\ CO_3$	Percent Soda Salt
I9	5.05	I.40	93.55
20	6.63	2.I2	9I.25
2I	5.45	2.90	9I.65
22	5.I9	I.86	92.95
23	6.57	I.69	9I.74
24	8.I2	I.68	90.20
25	7.90	I.60	90.50
26	8.50	I.I5	90.80
27	8.00	I.50	90.50
28	II.30	I.95	86.75
29	I2.09	2.II	85.80
30	I0.80	I.92	87.28
3I	9.02	2.06	88.92
32	5.92	I.67	92.4I
33	6.3I	I.67	92.02
34	7.67	I.88	90.45
35	7.29	I.93	90.78

[illegible]

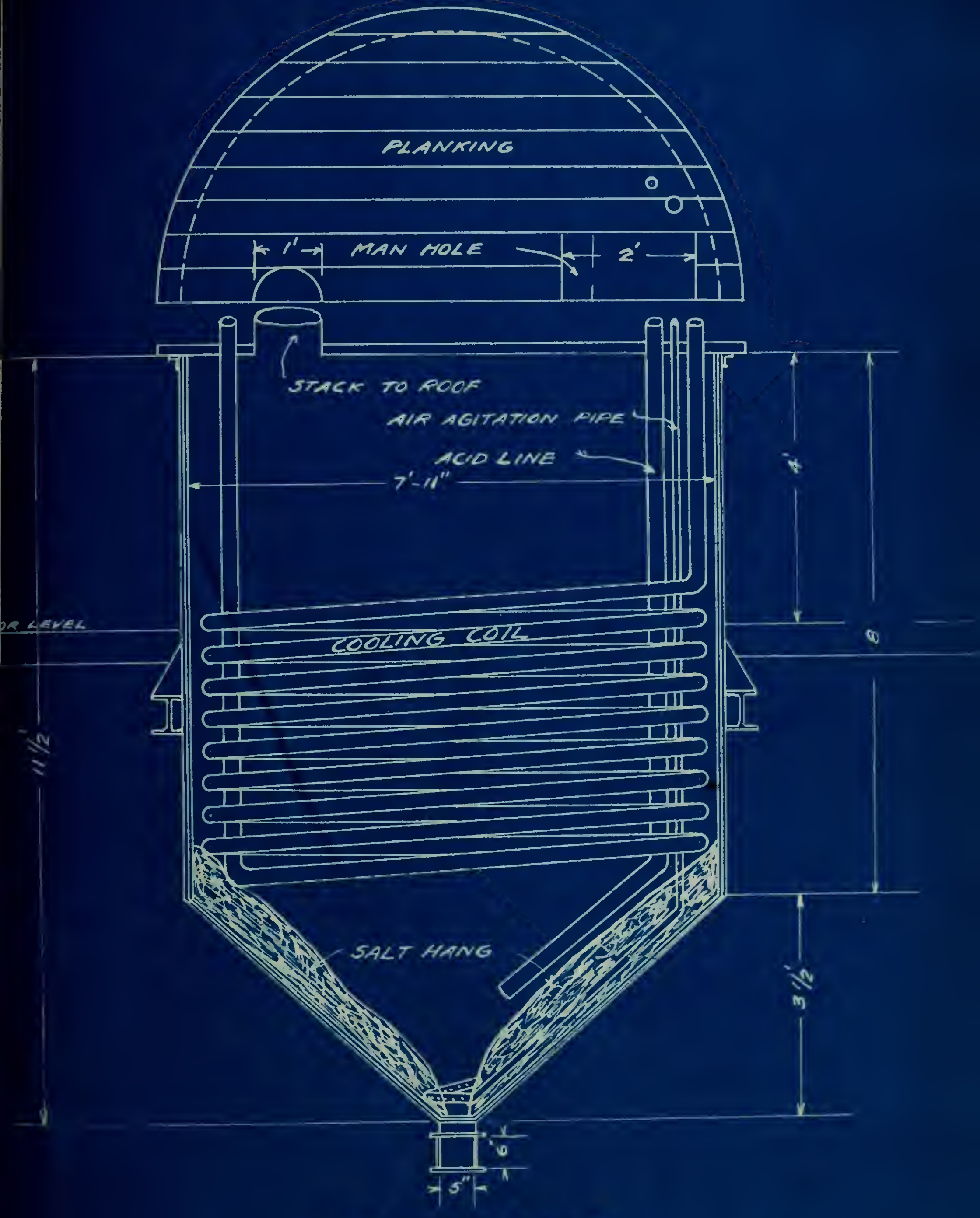
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

-FUSION TABLE - ANALYSIS of SODA SALT (dry basis) cont'd..

No.	Percent $Na_2 SO_4$	Percent $Na_2 CO_3$	Percent Soda Salt
36	6.62	I.69	9I.69
37	9.66	I.57	88.77
38	7.85	I.50	90.65
39	7.II	2.03	90.86

The LIBERATION of CRUDE PHENOL and the RECOVERY of PHENOL in the WASTE LIQUOR.

After a fusion was finished with the fusion room, it was blown to a so-called separator, or cone - bottom acidulating tank in the separating room, where it was agitated with air and diluted with cold water to about 25° Be'. A lead cooling-coil and cold water of dilution brought the temperature to 60° C. After the correct Beaume' had been obtained (with agitation and cooling water on) 40° Be'. sulphuric acid was dropped slowly beneath the surface of the diluted fusion until a sample of the same showed faintly acid with phenolphthalein. Agitation was then shut off and the sulphite, which was formed in the fusion kettle along with sodium sulphate formed during acidification, settled to the bottom of the separator, and the liberated phenol rose to the surface and floated as an oily liquid. After an hour or so the salts and waste liquor


PLANKING
1'
MAN HOLE
2'
STACK TO ROOF
AIR AGITATION PIPE
ACID LINE
7'-11"
4'
OR LEVEL
COOLING COIL
8'
11 1/2'
SALT HANG
3 1/2'
6"
5"

- SEPARATOR -

SCALE - 1' = 1/2"

R. D. Parrott '19.

were drawn off at the bottom and pumped to the waste recovery building and the phenol was allowed to drop to the crude storage. There was provided a sight glass at the lower end of the cone so that the operator could make the cut from waste liquor to phenol without delay and waste.

$$\underset{3124}{C_6H_5ONa} + \underset{1322}{H_2SO_4} \rightarrow \underset{2531}{2\,C_6H_5OH} + \underset{1915}{Na_2SO_4}$$

- TIME REACTION -

For a time acidulations were controlled by the Starch-Iodate method of indicating sulphurous acid or SO_2. It was found that the fusions were acid with SO_2 to phenolphthalein 5-10-15 minutes before the Starch Iodate indicated acidity. At this time a determination of SO_2 was made on the waste liquor. A composite sample of a day's run gave 4.55 percent of free and 5.13 percent of the total SO_2.

A previous "Time Reaction" experiment, carried out by myself, will explain this

time interval before acidity was apparent with Starch-Iodate.

"Prepare one solution by dissolving 1.8 grams of iodic acid of the equivalent amount of potassium iodate in one litre of water. Prepare a second solution with .9 grams of $Na_2 SO_3 . 7 H_2O$, 5 grams of 10 percent sulphuric acid and 9.5 grams of starch in one litre of water. Measure 100 cc., of each solution, into separate breakers. Mix these two 100 cc. portions at a definite instant and note the secondsuntil a deep blue color suddenly appears. Repeat for a check. Then make dilutions of the solutions to 4/5, 3/5, 2/5, and 1/5 of their original strength, and determine the elapsed time before the blue coloration appears as above. The results are reproducible and comparable only when the temperature of the solutions does not vary appreciably. (18° C.)

Dilution of	Time
1	:30"
5/4	:54"
5/3	1':54 4 5"
5/2	4':53 1 2"
4	14:40"
5	26':40"

"After the 5/3 dilution, or starting with the 5/2 dilution, the time was taken at the first change in color which was pink. This pink turned to deep blue (of the first three observations) after three or four seconds had elapsed. The fourth and fifth dilutions did not take on the blue color at all until one hour had elapsed and then very slowly.

"If a solution of iodic acid is added drop by drop to an aqueous solution of sodium sulphite acidified with sulphuric acid, the solution first remains colorless.

$$3\ H_2SO_3 + HIO_3 \rightarrow H_2SO_4 + HI.$$

"With further addition of iodic acid all the sulphurous acid becomes oxidized, the reduction continuing at the expense of the hydriodic acid which has been formed.

$$HIO_3 + 5HI \rightarrow 3H_2O + 3I_2$$

"Thus if an acidified solution of sulphite is treated with more than a mole of iodic acid a separation of iodine occurs; if the solution is concentrated, this separation

takes place immediately; if dilute, only after some time and then suddenly and completely.

"This very remarkable retardation reminds one of the phenomena of super-cooling, super-heating, and super-saturation, but it is different inasmuch as the reaction takes place in a homogeneous medium and is not followed by separation of material in another state of aggregation."

From the crude storage the crude phenol was pumped to dehydrating stills preparatory to vacuum distillation.

A fusion was diluted to 25° Be'. because at this dilution a cleaner and quicker separation of the waste liquor and crude phenol took place. This measurement of Beaume' was taken after the volume had been well agitated and the excess sulphite was in suspension. At 68.3° C. phenol and water are completely miscible in all proportions, and it was for this reason that the temperature of the diluted fusion was lowered to 60° C. or thereabouts to allow for a fair margin of

safety. With pure phenol in contact with water at 60° C. 100 grams of the phenol layer will contain 55 grams of phenol (55 percent) and 100 grams of the water layer will contain 17 grams of phenol (17 percent). In the separator with the concentrated salt liquor (25° Be'). there was enacted a salting-out effect to the extent of about 80 percent phenol in the phenol layer and 10 to 11 grams per litre in the waste liquor layer.

This temperature control was not strictly adhered to and consequently, now and then, an acidified fusion refused to separate into the phenol and waste liquor layers. Generally a little cold water added lowered the temperature and broke the miscibility.

Once in a great while an acidified fusion would make a poor separation. The phenol would come to the surface in the form of little independent globules or curds. A sample of this material when dropped into distilled water (or tap water) rapidly sunk

to the bottom and when shaken rolled about like little globules of oil. If a little acid was added and the mixture shaken and then saturated with common salt, the phenol gradually rose to the surface.

As with the sample, on adding more acid to the curdy separation in the separator and applying air agitation and then allowing to settle once more, the phenol would rise to the surface in the usual way. I believe this curdy separation was due to the solution of soda salt in the phenol, for since then great quantities have been found in the residue of the stills, and soda salt could not get into the stills unless it was contained in the crude phenol.

After the air agitation was shut off and the acidified fusion had been allowed to become quiet one would find a bank of sulphite and sulphate in the bottom of the separator, waste liquor above the sulphate, and a layer of crude oily phenol on the surface of the waste liquor. The waste liquor was run

off and pumped to the recovery building. Then the phenol was dropped to the crude storage after which the salt was flushed down and also pumped to the recovery building.

Considerable trouble was experienced with freezing of the waste liquor lines from the separators to the recovery building. This was especially true in cold weather. These lines were made up of lead pipes run in iron pipes. Generally by playing a jet of steam on the outside of the pipes one could loosen up the heavy solidified matter inside, but should this fail the lines had to be taken apart and steamed out with high pressure steam.

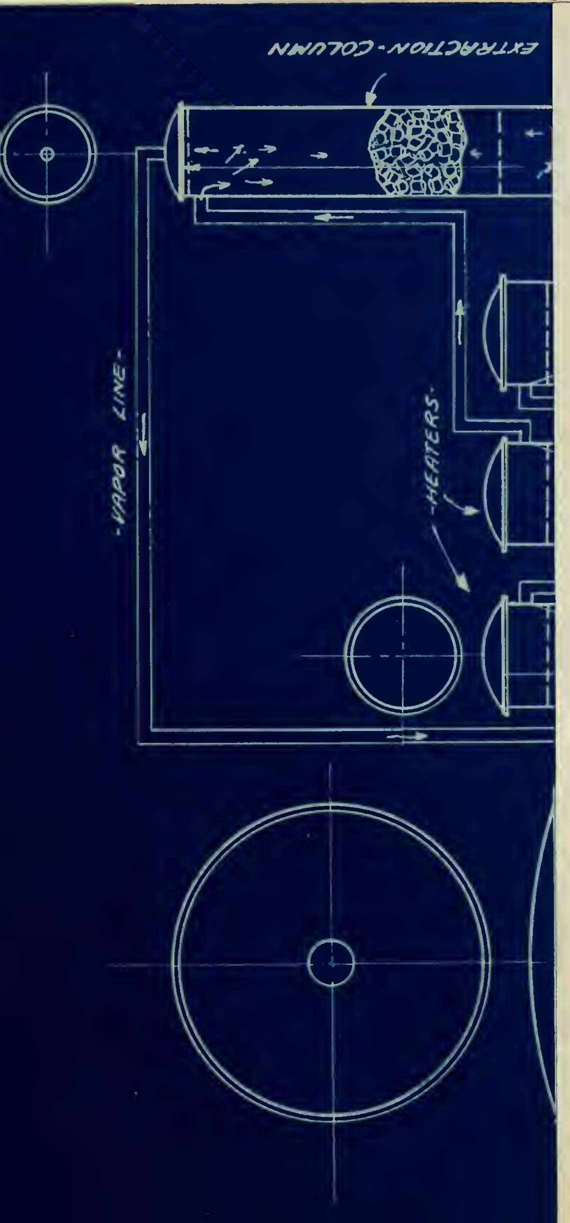
The waste liquor and the salt were received in two large storage tanks in the recovery building. The heavier salt liquor was pumped off at the bottom of these tanks (as it is needed) to the lime tubs. The cleaner liquor above the salt was pumped through two heaters (A and B) to the top of a battery of three columns. The liquor flowed down through a nipple packing and met an 80-pound jet of up-coming steam. The phenol

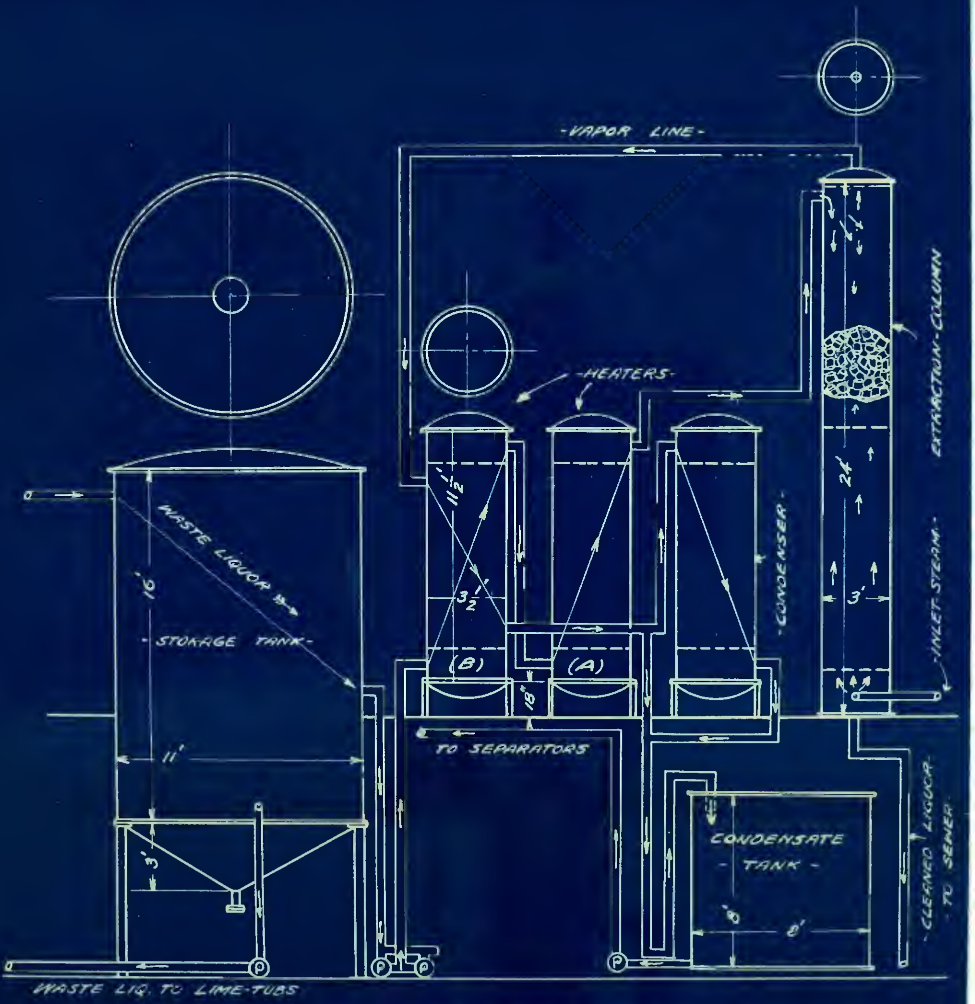
was cleaned out of the liquor, virtually, by steam distillation. The cleaned liquor then flowed out the bottom of the columns to the sewer. A second battery of three columns and two heaters was available for use so that the first battery could be steamed and flushed out without interrupting operation. Initially it was proposed to absorb the phenol from the distilled waste liquor vapors by circulating a caustic solution through the columns. The great amount of SO_2 (5 percent) in the waste, however, soon neutralized the caustic and made it worthless.

The steam traveled up the column, cleaned the waste liquor and then passed down throuth a water-cooled condenser, the condensate being received in tanks below the columns. On the way down the steam passed through the heater "B" where some of it was condensed. This condensate dropped into a seal-leg and was syphoned to the receiver with the rest of the condensate.

The temperature of the liquor in the storage tanks was about 50° C., that entering the

live heater 75° C., and that entering the columns about 90° C. The temperature of the


EXTRACTION - COLUMN
VAPOR LINE
HEATERS


-VAPOR LINE-
-HEATERS-
EXTRACTION-COLUMN
-CONDENSER-
-INLET-STEAM-
WASTE LIQUOR
-STORAGE TANK-
16'
11'
3'
11½'
3½'
18"
(B)
(A)
24'
3'
TO SEPARATORS
CONDENSATE
-TANK-
8'
8'
-CLEANED LIQUOR TO SEWER-
P
WASTE LIQ. TO LIME-TUBS

-EXTRACTOR-DETAIL- SCALE. 1'=3/16"

R. D. Parrott '19.

live heater 75° C., and that entering the columns about 90° C. The temperature of the cleaned liquor to the sewer was 100-101° C.

About 5500 gallons of waste liquor were cleaned per hour with about 98 percent efficiency. The phenol condensate contained about 60 grams per litre and amounted to 800-900 gallons per hour. This condensate was pumped to the separators as it was formed, and served to help make dilutions.

Formerly the liquor to the columns was pumped off at the bottom of the storage tanks and considerable trouble resulted. Decomposition matter of the fusions mixed with the salts of the waste liquor coated the nipple-packing, and all but clogged the columns except for a small vent up to the center. This coating being tarry and insoluble could not be steamed nor washed clear of this packing but had to be removed by hand. This meant opening up the column. It was found that a very good way to clean them, when needed, was to put them in a concrete mixer and roll them about with

plenty of flush water and steam. The heaters also became clogged with this matter and it was with great difficulty that these were poked and chipped clean. Later a steam jet applied now and then to the salt banks had a tendency to break them and flush them through. The application of these steam jets, every 24 hours, increased the life of the heaters over that of the average.

Liquor from the separator room to the recovery building, from the storage tanks to the columns, and from the storage tanks to the lime tubs was handled by centrifugal pumps. The pump which delivered the liquor to the lime tubs ran all the time. When the liquor was needed at the tubs the proper valve was opened, and when not it was closed. When it was closed, the pump carried no load and needed no attention except oiling and packing. Initially Worthington piston pumps were used throughout the recovery building but later were replaced with fool-proof centrifugals. If by some carelessness a valve was closed on the

delivery line of a plunger pump, something had to give and this was generally the packing and sometimes the pump itself. Later the centrifugal pumps in duplicate were used throughout the building.

-EXTRACTION RECORD-

Time	Temp. at Storage	Temp. to Preheater "A"	Temp. to Column	Inches of Condensate	Tests to Sewer
8:00	56.0	76.0	92.0		O.K.
8:30	53.0	75.5	86.0		"
9:00	52.5	83.0	90.0		"
9:30	54.0	78.0	92.0		"
I0:00	57.0	75.5	84.0		"
I0:30	63.0	78.0	94.0		"
II:00	56.0	77.0	97.0		Trace
II:00	54.0	69.0	86.0		"
I2:00	48.0	67.0	84.0		O.K.
I2:30	47.5	66.0	82.0		"
I:00	48.0	68.0	89.0		"
I:30	49.5	70.0	92.0		"
2:00	5I.0	75.0	92.0		"
2:30	52.0	76.0	90.0		2
3:00	50.0	75.0	93.0		"
3:30	52.0	75.0	9I.5		"

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

- DISTILLATION of the CRUDE PHENOL -

From the crude storage the 80 percent crude phenol containing salts and water was pumped to dehydrating stills with a centrifugal pump. Here 80 percent of the contained water is removed at atmospheric pressure with 135 pounds of steam on the coils.

In the new plant the dehydrating capacity was great enough to dehydrate all the 80 percent crude produced, preparatory to the vacuum distillation. In the old plant the capacity was only about one-third as large as it should have been.

The idea of dehydration preparatory to vacuum distillation was to shorten the time of vacuum still operation, thereby making a smaller vacuum capacity do the work of a greater vacuum capacity using crude without preliminary dehydration. This makes for a saving in space, time and labor.

-CRUDE STILL RECORD-

Date ....

Run No. - - - - - - -.____.Crude Still No. - - - - - - - - - - -____ .

Time Charged -______.

Time Run Started - - - - -_____. Stopped - - - - - - - _______.

Inches Before - - - - - - _____. After - - _____. Charge _____.

Time. Kettle Temperature.

Remarks: Discharged to - - - - - - - - - - - - - - - ___________.

The time to dehydrate a batch of 80 percent crude was about 5 hours, that for the vacuum distillation of the dehydrated material 6 or 7 hours. If the complete distillation had been made in the vacuum still, the time required would have been 12 to 14 hours.

The vacuum distillation apparatus (Badger) consisted of the still body, column, dephlegmator, condenser, water or forerun receiver, 2 enameled phenol receivers located in the phenol weigh room (one to be used while the other was being emptied), watch glass, and wet vacuum pump with connecting vapor lines.

The still body was charged with crude to within about 12 to 18 inches of the top by means of a cast-iron centrifugal pump. Too great a charge will boil over. The vent in the kettle was left open, the valve to the column was opened and a full stream of water was run to the dephlegmator and condenser. The steam at 135 pounds was put on the kettle coils and allowed to remain there 'till the column was hot to the touch, after which time it was shut

off tight and then again applied slowly to avoid a rush of vapor. As the water started trickling through the watch glass the volume of steam was increased till the flow of condensate was about the size of the first two fingers. As the flow of condensate decreased the water on the dephlegmator was decreased both in rate of flow and height until finally it was dry and full steam was on the kettle coils. When the flow of condensate stopped under these conditions, the steam was shut off and the contents of the still allowed to settle for a few minutes. At this point in the process the bulk of the water was off.

From now on the distillation proceeded under vacuum. All air vents were closed, the vacuum valves on the forerun and phenol receivers were opened and the vacuum pump started slowly. The dephlegmator was filled again to check a vapor rush. In 15 to 20 minutes the vacuum had reached 24 or 25 inches of mercury and the condensate flow had started again. To increase this flow the volume of

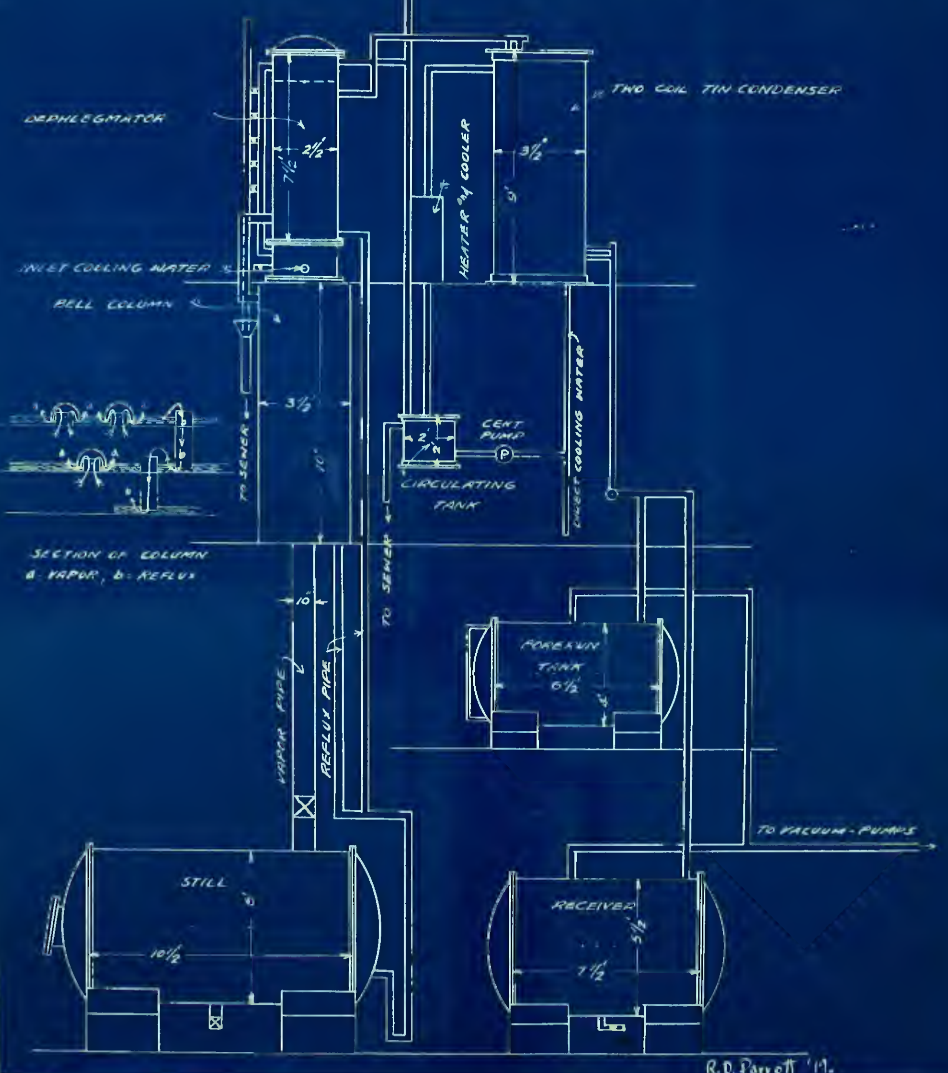
-BADGER-

-DISTILLATION-APPARATU

SCALE-1' = 1/4"-

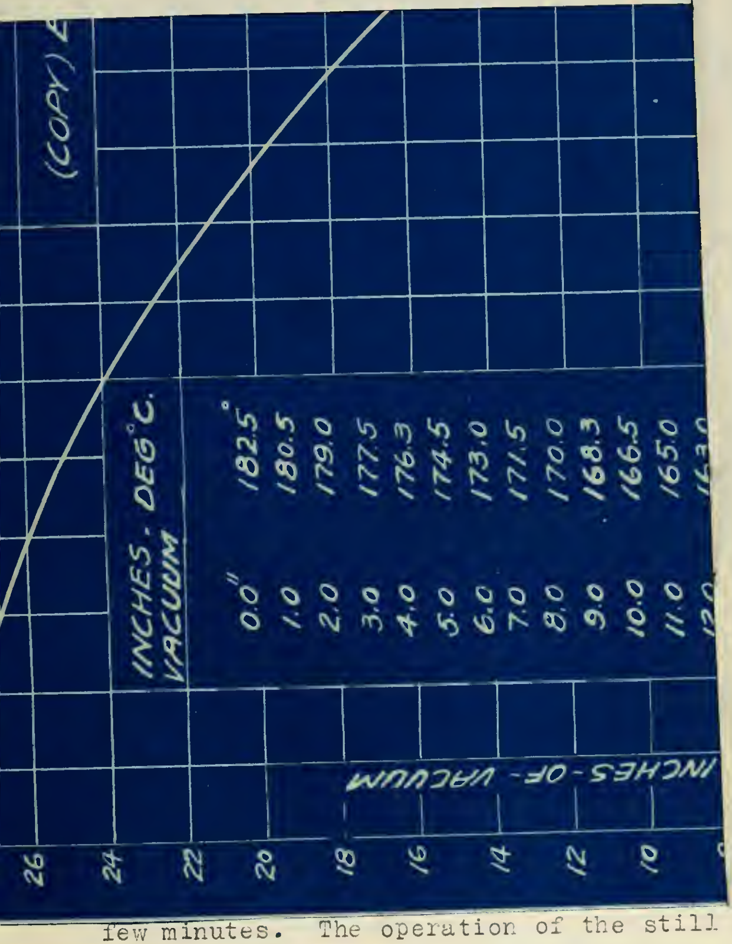
-BADGER-
-DISTILLATION APPARATUS-

SCALE - 1' = 1/4" -


DEPHLEGMATOR
TWO COIL TIN CONDENSER
2½'
7½'
3½'
9'
HEATER and COOLER
INLET COOLING WATER
BELL COLUMN
a
b
3½'
10'
TO SEWER
CENT. PUMP
P
2'
4'
CIRCULATING TANK
INLET COOLING WATER
SECTION OF COLUMN
a- VAPOR, b- REFLUX
10"
TO SEWER
VAPOR PIPE
REFLUX PIPE
FORERUN TANK
6½'
4'
TO VACUUM-PUMPS
STILL
6'
10½'
RECEIVER
5½'
7½'
R.D. Parrott '19.

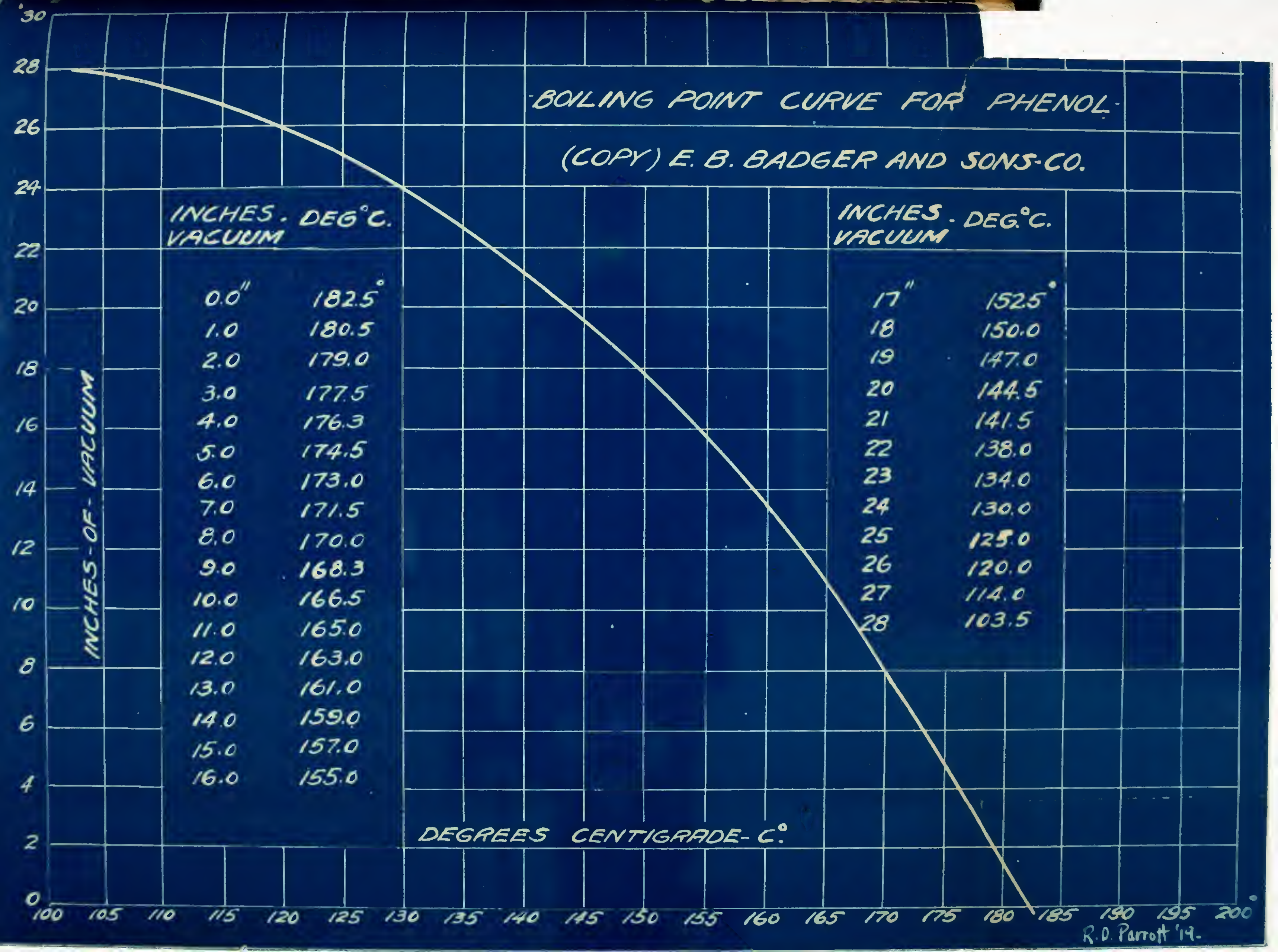
steam was increased and the water decreased on the dephlegmator. One who was familiar with the individual stills could almost bridge the gap from atmospheric to vacuum distillation and maintain a flow. There was a break with the best of operation but of short duration. This forced distillation means more phenol in the forerun receiver. As the temperature on the kettle indicated phenol in the kettle vapors, the direct water was cut off and the circulating pump (centrifugal) was started. The hot vapors passing through the condenser warmed the circulating water to 42-45° C. and by running cooling water through the cooler this temperature was maintained.

After the circulating pump was started one had to watch closely for the water-free phenol flow. Samples were taken in the melting tubes and the melting points were noted and when the correct melting point was reached the receivers were switched from forerun to phenol. This water-free phenol was obtained after the cooling water had been



INCHES. VACUUM	DEG C.
0.0"	182.5°
1.0	180.5
2.0	179.0
3.0	177.5
4.0	176.3
5.0	174.5
6.0	173.0
7.0	171.5
8.0	170.0
9.0	168.3
10.0	166.5
11.0	165.0
12.0	163.0

few minutes. The operation of the still was the



BOILING POINT CURVE FOR PHENOL

(COPY) E. B. BADGER AND SONS-CO.

INCHES - VACUUM	DEG°C.
0.0"	182.5°
1.0	180.5
2.0	179.0
3.0	177.5
4.0	176.3
5.0	174.5
6.0	173.0
7.0	171.5
8.0	170.0
9.0	168.3
10.0	166.5
11.0	165.0
12.0	163.0
13.0	161.0
14.0	159.0
15.0	157.0
16.0	155.0

INCHES - VACUUM	DEG°C.
17"	152.5°
18	150.0
19	147.0
20	144.5
21	141.5
22	138.0
23	134.0
24	130.0
25	125.0
26	120.0
27	114.0
28	103.5

R. D. Parrott '19.

circulating two or three hours. The melting point was taken at intervals to keep a check on the distillation. A drop in the melting point may have indicated a water leak or poor dephlegmation. Too great a flow of condensate with too great a temperature caused considerable quantities of phenol vapors to be sucked over the goose neck into the vacuum pumps and lost. (A maximum safe temperature was 75° C.) These vapors also had a tendency to crystallize and clog the longer vapor lines. As the phenol flow decreased, indicating the approach of the end of the distillation, the circulating water was allowed to warm up to 50° C. When the flow stopped the receivers were switched and steam was blown into the base of the column to remove any dilute phenol to prevent clogging the column with crystals.

If the still was charged with dehydrated material, the vacuum was applied immediately and water-free phenol flowed in a few minutes. The operation of the still was the

same as with 80 percent crude material.

A silver coil was provided in the phenol receiver on which two or three pounds of steam were maintained to keep the contents liquid.

Silver or block-tin condensers were employed. If tin was used a greater area was necessary. The latter gave less trouble from leaks and never collapsed.

Two receivers were fitted to each still and while one was in use the other was being emptied into drums. The phenol was packed in tared drums. Precision platform scales were employed, reading in fractions of a pound. Two sizes of drums were used holding 242 and 780 pounds net weight. Phenol for export was put in the 242-pound drums and those in turn were put in barrels and packed with sawdust.

A normal charge of 80 percent crude material was 1850 gallons, of dehydrated material 1350 gallons. The yield per distillation averaged about 11,000 pounds of water-free phenol.

-DISTILLATION RECORD-

Date- I2-7-'I7 .

Series- I005 Time Start- 7:05 A.M. Inches Before--------8I.5 .
Still No. 3 Time Stop- 7:I5 P.M. Inches After --------35.0
Crude Run No. Inches Charged ------46.5

Time	Temperature Kettle	Temperature After Def.	Phenol Tests	Inches Vacuumn Kettle	Inches Vacuumn After Def.	Steam Pressure .
7:30	97	72				I00
8:00	96	96				"
8:30	97	97				"
9:00	97	96				"
9:30	97	95				"
I0:00	I06	96				I30
I0:30	I07	96				"
II:00	I08	96	°C.			"
II:30	II3	96				"
I2:00	II8	84		I9.0	I8.0	"
I2:30	II8	II0	35.2	24.0	23.0	"
I:00	I25	III	37.7	23.0	24.0	"
I:30	I26	I27	37.4	23.0	2I.0	I35
2:00	I29	I30	40.6	2I.5	2I.0	"
2:30	I3I	I32	40.6	2I.0	20.0	"

-DISTILLATION RECORD- cont'd.

Time	Temperature Kettle	Temperature After Def.	Phenol Tests	Inshes Vacuum Kettle	Inshes Vacuum After Def.	Steam Pressure .
3:00	I34	I36	40.6	20.00	I9.0	I35
3:30	I37	I37	40.6	20.0	I6.0	I40
4:00	I38	I38	40.6	2I.0	I5.0	I35
4:30	I30	I37	40.6	2I.0	I6.0	"
5:00	I28	I3I	40.6	20.0	I7.0	"
5:30	I28	I29	40.6	22.0	I9.0	"
6:00	I20	I23	40.7	25.0	2I.0	"
6:30	II0	II5	40.6	26.0	2I.0	"
7:00	II0	II5	----	26.0	2I.0	"
7:I5	II0	II5	40.6	26.0	2I.0	"

Residue in Still before--- I4"" After--- I8"
Pounds of C. P. Phenol - - - - - - - - - -I0228..
Time Start Phenol to Receiver - - - I:00 P. M .
Received in the Warehouse - - - - - 8:00 P. M .
Batch Test - - - - - - - - - - - - - - - -40.5°C.

- TREATMENT of STILL RESIDUES -

After a still had been charged two or three times there remained a residue of salty, tarry, phenolic matters which contained too much phenol to flush to the sewer, so it was washed out and pumped to the separating room to be dealt with there. This material for a considerable time was mixed in with regular acidifications, and in due time was charged back to the still. There finally resulted an accumulation that was little less than tar, which coated the still coils and was bothersome in general. An attempt was made to filter a sample of this material through a small experimental Sweetland Press, both hot and cold. Almost immediately the press leaves became coated and the filtrate flow all but stopped. This was with a pressure of 50 pounds of air.

Several samples identical to the above were mixed in different proportions with the Oliver gypsum cake ($Ca\ SO_4 .\ 2\ H_2O$) and then put through the press both hot and cold.

These did not give the porous cake as was expected of them and results were the same as above.

After these experiments gave no promising results, I tried leaching the "muck" and the following is the report of the simple experiment.

"A sample of "muck" was filtered on a Beuchner funnel with suction. The filtrate showed 45 cc. of phenol layer and 55 cc. of waste liquor layer in a 100 cc. graduate. This afforded in a rough way an estimate of the phenol content of the filtrate.

"Then 100 cc. of the above "muck" were made up to 1000 cc. with cold water (21° C.), thoroughly agitated and allowed to settle. A greasy slimy precipitate settled to the bottom. The supernatant liquor was then decanted off and 100 cc. put into a graduate.

"This 100 cc. of phenol leach was salted for phenol and 5 cc. separated out on top. In the 1000 cc. volume, 9 parts of (100 cc. each) leach and 1 part of sludge made the total

volume. Therefore, 9 parts of supernatant liquor or leach at 5 cc. phenol each makes 45 cc. total phenol layer.

"Hence if the sludge or tarry matter could be leached and the leaching allowed to settle, practically all of the phenol could be obtained in the upper clear waste liquor and the settled sludge could be dropped to the sewer."

This procedure was carried out for some little time until greater production made it impossible due to the lack of separating space. The still residues were then pumped directly to the storage tanks in the recovery building, only now and then making a leach.

- STILL MEASUREMENTS -

I took a few measurements on still foreruns and phenol in the vacuum pumps which are as follows:

PHENOL in VACUUM PUMPS

Samples of contents of the water-seal tanks were taken at regular intervals after the tanks were flushed clear of phenol (by test) and the feed water shut off (constant volume). Phenol content was estimated by the tri-brom method.

Still #3 Tank = 6.25 cu.ft. = 390# H_2O

Time	T.B. Phenol	Percent Phenol
1 hour	.019	"
2 "	.035	"
3 "	.061	"
Average	.0191	.0543

Estimating a still run (vacuum on) at 7 hours duration, we get

390 X .000543 X 7 = 1.48 pounds loss.

Still #1 Tank = 9.8 cu.ft. = 612# H_2O

Time	T.B. Phenol	Percent Phenol
1 hour	.04	"
2 "	.082	"
3 "	.130	"
Average	.043	.024

[illegible]

[illegible]

[illegible]

[illegible]

Estimating a still run (vacuum on) at 7 hours duration, we get

612 X .00024 X 7 = 1.039 pounds loss.

Still #2 Tank = 7.05 cu.ft. = 440.5# H_2O

Time	T.B. Phenol	Percent Phenol
1 hour	.085	"
2 "	.160	"
3 "	.221	"
4 "	.351	"
Average	.082	.0266

Estimating a still run (vacuum on)at 7 hours duration, we get

440.5 X .000266 X 7 = 1.43 pounds loss.

Still #4 Tank = 10.3 cu.ft. = 643# H_2O

Time	T.B. Phenol	Percent Phenol
1 hour	.047	"
2 "	.082	"
2-1/2"	.101	"
Average	.042	.0238

Estimating a still run (vacuum on)at 7 hours duration, we get

6.43 X .000238 X 7 = 1.07 pounds loss.

Results:

At 7 hours as a still run (vacuum on) the losses in the pumps are as follows:

Still No.	Pounds Loss
No. 1	1.03
No. 2	1.43
No. 3	1.48
No. 4	1.07

Several foreruns were sampled and tested for phenol and their volumes determined. The liquor level in the tanks was noted and the volumes estimated from a calibration. After the volumes were estimated the foreruns were blown to the separator room, well agitated and sampled. The phenol was estimated by the Iodine method.

Measurements on stills 1 and 2 were constant while those on 3 and 4 were irregular. Stills 1 and 2 were operated by one man and 3 and 4 by another man. Also stills 1 and 2 were fitted with silver tube condensers whereas 3 and 4 were fitted with tin condensers. The latter became overheated often for the lack of water. I have seen them steam and still a greater quantity of water was being applied to them than to the silver tube condensers on stills 1 and 2.

-STILL FORE-RUNS-

	#I	#I	#I	#2	#2	#2
Still and series Number	I390	I439	I446	I398	I4I4	I460
Still Charge in Gallons	I905	I925	I925	I945	I905	I825
Fore-Run in Gallons	546	5I9	428	539	490	505
Grams of Phenol per Liter in Fore-Run	I70	I60	I74	I63	I33	I45
Water-Free Phenol Produced in Pounds	7282	II473	I0456	I0I39	I2479	II300
Phenol in Fore-Run in Percent	9.6	5.7	5.6	6.7	4.2	5.I
Phenol in Fore-Run in Pounds	772	690	6I9	732	542	609

	#3	#3	#3	#3	#4	#4
Still and Series Number	I395	I4I2	I399	I455	I402	I454
Still Charge in Gallons	I985	I885	I885	I805	I5I5	I905
Fore-Run in Gallons	230	5I9	620	546	58I	46I
Grams of Phenol per Liter in Fore-Run	402	460	460	I87	447	278
Water-Free Phenol Produced in Pounds	II576	I0759	I0690	II867	8452	II887
Phenol in Fore-Run in Percent	6.2	6.0	2.I	7.I	20.4	8.2
Phenol in Fore-Run in Pounds	772	690	233	849	2I63	I062

- METHODS of ANALYSIS and CONTROL -

The actual sampling of products was done by the operators but the shift chemists were on the "job" to see that this sampling was done correctly and at the right time.

The sulphonations were sampled as the operator or shift chemists saw fit, other samples being taken to the laboratory immediately for testing.

Oliver and Shriver presses and the evaporators were sampled every hour. The extractors in the recovery building were sampled every half hour. The phenol stills were tested about every half hour or as the operator saw fit in order that a close check could be kept on them. Final phenol samples were obtained in the weigh room.

- TESTS ON SULPHONATION MIXTURES -

FREE BENZOL

200 grams of the sulphonation mixtures are diluted with about 500 cc. water and placed

in a 1000 cc. round-bottomed flask. After connecting with a condenser, the mixture is boiled and the condensate collected in a graduated cylinder. When about 75 cc. are distilled over, the distillate is transferred to a burette and the cc. of benzene measured.

$$\text{Lbs. Benzene} = \frac{(\text{cc.})\,(.88)\,(6600)}{200}$$

$$= (\text{cc.})\,(29.04)$$

$$\text{Percent Benzene loss} = \frac{(\text{Pounds Benzene})\,(100)}{2100}$$

$$= (\text{Pounds Benzene})\,(.04762)$$

Using 4500 pounds of 102% acid, 2100 pounds of benzene, and per directions of analysis, one can read the percent loss from the following table:

cc. Benzene	% Loss	cc. Benzene	% Loss
.1	.14	.9	1.26
.2	.28	1.0	1.40
.3	.42	1.1	1.54
.4	.64	2.0	2.80
.5	.70	3.0	4.20
.6	.84	4.0	6.40
.7	.98	5.0	7.00
.8	1.12	6.0	8.40

- SULPHONE LOSS -

A composite of the day's sulphonations is made taking 100 cc. of each sulphonation mixture; this same composite is used for determining the efficiency of sulphonation. 200 cc. of the composite are diluted with 500 cc. H_2O and the benzol is distilled off as in the free benzol test. The mixture is cooled, filtered, and the precipitated sulphones are thoroughly washed with cold water until free from H_2SO_4. The filter paper and sulphones are dried in an air oven at 80° C. (no higher). When dry the sulphones are scraped off the filter paper and weighed.

BENZENE LOSS in POUNDS as SULPHONE

$$= \frac{(\text{Grams Sulphone})\ (7138)\ (.6600)}{200}$$

$$= (\text{Grams Sulphone})\ (23.56)$$

Soda Salt Loss = (Benzene Loss) (2.308)

Percent Loss as Benzene = (Pounds Benzene) (0.4762)

- ACIDITY -

10 to 15 grams of the sulphonation mixture are weighed out (in a 100 cc. Beaker) on the analytical balance and then diluted to 500 cc.. 25 cc. of the diluted mixture are taken and titrated with N/2 NaOH using phenolphthalein as an indicator.

Percent Acidity =

$$\frac{\text{Log cc. of NaOH - Log (factor N/2 NaOH - Log 20)}}{\text{Log of weight of sample}}$$

$$= \frac{\text{Log cc. of NaOH - Log (factor N/2 NaOH - 20)}}{\text{Log of weight of sample.}}$$

METHOD for DETERMINING the EFFICIENCY of SULPHONATIONS

A composite sample of the number of sulphonations dropped during a 24-hour day is obtained by taking 100 cc. of each sulphonation mixture just before it is dropped. Fifty grams (weighed on analytical balance) of this composite sulphonation mixture are weighed in a

100 cc. Beaker, then transferred to a 500 cc. beaker, and diluted to about 2-300 cc. The solution is brought to a boil to get rid of the benzene, after which it is cooled and made up to 500 cc. in a volumetric flask.

The 500 cc. are shaken well and 50 cc. of this solution are taken and treated (cold) with excess dry $Ba CO_3$. About .5 gr. is added and the mixture is brought to a boil. This mixture is cooled, diluted to 500 cc. and filtered. 100 cc. of the filtered solution are boiled and then treated with dilute $H_2 SO_4$.

The resulting precipitate is filtered on quantitative filter paper, ignited, and weighed as $Ba SO_4$.

For 4500 lbs. acid and 2100 lbs. benzol

Present Efficiency = Grams $Ba SO_4$ x 210.

PRESS LOSS DETERMINATION

Samples are taken every hour along the scraper of the Oliver filters to obtain a composite sample of a day's run. The method of sampling the press cake of the Albright & Nell

and Shriver presses is to take two or three samples from each leaf of the press and make a composite sample.

PRESS LOSS

The samples obtained from the Oliver filters and from the other presses are mixed and quartered. About 50-60 grams of a representative sample are heated on a watch glass in an oven kept at a temperature between 100° C. and 110° C. An hour or more is required to drive off all the moisture. Two grams (weighed accurately) of the dried cake are extracted with alcohol in a Soxhlet extraction apparatus for three to four hours. The solution of salt in alcohol is filtered into a tared beaker, washed with alcohol, and the alcohol is then driven off by evaporation. The residue is regarded as the amount of soda salt in two grams of dry press-cake. The total weight of the dry press-cake from one sulphonation is 5800 pounds; this weight is calculated in the following manner:

Benzol used - - - - - - - - 2100 pounds

H_2SO_4 used - - - - - - - - 4500 pounds

of 102% or 4590 of 100 % acid.

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$$

2100#   2636#   4252#

4590 - 2636 = 1954 lbs. acid to be neutralized with lime.

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O$$

1954# $\underline{\underline{3430\#}}$

$$C_6H_5SO_3H + Ca(OH)_2 \rightarrow (C_6H_5SO_3)_2Ca + 2H_2O$$

4252#   4763#

$$(C_6H_5SO_3)_2Ca + Na_2SO_4 \rightarrow$$

3512   1408

$$2C_6H_5SO_3Na + CaSO_4 \cdot 2H_2O$$

$\underline{\underline{1705}}$

$$(C_6H_5SO_3)_2Ca + Na_2SO_3 \rightarrow$$

1207   430

$$2C_6H_5SO_3Na + CaSO_3 \cdot 2H_2O$$

$\underline{\underline{587}}$

(Only a partial conversion in the lime tubs)

3430	lbs.	$CaSO_4 \cdot 2H_2O$	(excess acid)
1705	"	"	(partial conversion)
587	"	$CaSO_3 \cdot 2H_2O$	(" ")
78	"	Foreign matter (in lime)	
5800	"	Total weight dry press cake per sulphonation.	

Having the weight of soda salt in the 2-gram sample of dry cake the total amount of soda salt in the press-cake per sulphonation may be obtained by the formula:

Total soda salt = (weight of soda salt in 2-gram sample) (2900).

-SODA PRESS LOSS- 2500 pounds wet cake (48 % H_2O) per press.

-Specific Gravity-

No. Presses.	I.001	I.002	I.003	I.004	I.005	I.006	I.007	I.008	I.009	I.010	I.011	I.012.
I	2.5	5.0	7.5	I0.0	I2.5	I5.0	I7.5	20.0	22.5	25.0	27.5	30.0
2	5.0	I0.0	I5.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0	55.0	60.0
3	7.5	I5.0	22.5	30.0	37.5	45.0	52.5	60.0	67.5	75.0	82.5	90.0
4	I0.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	I00.0	II0.0	I20.0
5	I2.5	25.0	37.5	50.0	62.5	75.0	87.5	I00.0	II2.5	I25.0	I37.5	I50.0

Explanatory: Theoretically a volume of 500 cc. of water to which is added .5 gram of soluble salt becomes of specific gravity I.00I (500.5 ÷ 500 = I.00I).

500 cc. of specific gravity I.00I = 500.5 grams; 500.5 grams minus 500 grams leaves .5 grams; .5 ÷ 453.6 = .00II and 500 ÷n453.6 = I.I . Then 2500 pounds ÷ I.I = 2273 units of 500 grams each. Therefor 2273 gxa .00II gives 2.5 pounds loss.

Procedure: 500 grams of wet cake (48 % moisture) are thoroughly mixed with 500 cc. of distilled water, filtered and the specific gravity taken(with the Westphal balance) of the filtrate. The table will then give the loss on the presses of cake when the cake amounts to 2500 pounds.

— (September,I9I7. R. D. Parrott.)

- ANALYSIS of SODA SALT -

A composite of the soda salt produced during the day's run is made by taking hourly samples of the heavy solution in the second cell of the evaporator; about 100 cc. of the soda salt solution are taken from the testing tube on the side of the evaporator. At the end of a day's run the composite sample is heated so that all the salt is in solution. About 200 grams of the composite are then evaporated to dryness, and finally heated at 100 to 120° C. for an hour. Two 10-gram samples are weighed out.

SAMPLE #1. EXCESS $Na_2 CO_3$

One of the above samples is placed in a beaker and dissolved in distilled water. The excess $Na_2 CO_3$ is titrated with standard HCl, after adding methyl orange for an indicator.

1 cc. N/2 HCl = .0265 gr. $Na_2 SO_3$.

SULPHATE

The insoluble matter left after the determination of $Na_2 CO_3$ is filtered off and

the filtrate is treated with excess HCl. It is then heated to boiling and the sulphate precipitated with Ba Cl_2. The hot precipitate is then filtered through an analytical filter paper, ignited and weighed as Ba SO_4 in a porcelain crucible.

$$Na_2\ SO_4 = \text{grms. Ba } SO_4 \times .609$$

Sample #2. CALCIUM

The second sample is dissolved in 100 cc. hot water and HCl is added to dissolve any insoluble matter. NH_4OH is added to alkalinity and then $(NH_4)_2\ C_2O_4$ is added; the mixture is boiled, filtered, and the precipitate is washed with hot water until all traces of free oxalate are removed.

The precipitate is transferred to a beaker by punching a hole through the bottom of the filter paper, while it still remains in the funnel, and washing the precipitate through the hole by means of hot water from a wash bottle; the paper is then washed with dilute $H_2\ SO_4$.

20 cc. (1:1) H_2SO_4 are added and solution is diluted with hot water to 300-400 cc.; then the solution is heated to boiling and titrated with N/10 $KMnO_4$.

1 cc. N/10 $KMnO_4$ = .002005 gr. Ca = .002807 gr. CaO.

It was suggested that if a sample of soda salt should be burned while drying at 100° C. the sodium sulphate might be unnecessarily high. In other words the soda salt in burning is converted into sulphate. (At 90° C. soda salt takes on a brownish charred-like tint). At any rate, to eliminate this possible error, a chart was worked out giving the specific gravity at 23° C. and the solid content of soda salt solutions. Then instead of weighing out a dry sample of soda salt, a measured volume of soda salt was taken for analysis. Upon close observation I could not detect any drop in the sulphate content after the procedure went into effect. The accuracy of the two procedures (dry and wet measures) was about equal when average care was exercised.

In one case it was an abused balance that was used and in the other a beautiful new Westphal.

From the following points a curve was made and a following table was made from the curve. (23° C.)

Sp.Gr.	Grams/Litre	Sp.Gr.	Grams/Litre
1.03	72.0	1.08	193.5
1.04	96.5	1.09	217.5
1.05	121.0	1.10	242.0
1.06	145.0	1.110	266.0
1.07	170.0	1.120	290.0

SPECIFIC GRAVITY of PURE
SODA SALT SOLUTION at 23° C.

Sp.Gr.	Grams/100 cc.	Sp.Gr.	Grams/100 cc.
1.050	12.00	1.071	17.25
1.051	12.25	1.072	17.50
1.052	12.50	1.073	17.75
1.053	12.75	1.074	18.00
1.054	13.00	1.075	18.25
1.055	13.25	1.076	18.50
1.056	13.50	1.077	18.75
1.057	13.75	1.078	19.00
1.058	14.00	1.079	19.25
1.059	14.25	1.080	19.50
1.060	14.50	1.081	19.75
1.061	14.75	1.082	20.00
1.062	15.00	1.083	20.25
1.063	15.25	1.084	20.50
1.064	15.50	1.085	20.75

SPECIFIC GRAVITY OF PURE SODA SALT SOLUTION at 23° C.

(continued)

Sp.Gr.	Grams 100 cc.	Sp.Gr.	Grams 100 cc.
1.065	15.75	1.086	21.00
1.066	16.00	1.087	21.25
1.067	16.25	1.088	21.50
1.068	16.50	1.089	21.75
1.069	16.75	1.090	22.00
1.070	17.00	1.09o	22.25

SODA SALT in EVAPORATOR CONDENSATE

A composite of the day's run is made by taking 100 cc. every hour. Two litres of the condensate are then evaporated to about 100 cc. in a large evaporating dish. The concentrated liquor is then filtered into a small tared evaporating dish, the large evaporating dish and filter paper being washed and the wash water added to it. It is then evaporated to dryness on a steam bath and weighed. Calculate results to pounds loss per gallon as follows:

$$\text{Percent loss} = \frac{\text{Grs. found X 100}}{2000}$$

Loss in lbs. gals. = 8.33 X percent loss.

The total gallons of condensate plus cooling water is arrived at theoretically (and was checked very closely practically).

4845 lbs. of soda salt at 95% (operation) = 4600#.
4600# at 1.25# per gallon evaporated to 4.25# per gallon means 2683 gallons of water evaporated. The condensate is cooled to 105° C. (about). Latent heat at 212° F. is 1077.5 B.T.U. Take water at 7.3° C. or 46° F. to 105° F. is 59 B.T.U.

$\frac{1077.5 \text{ X } 2638 \text{ X } 8.33}{59 \text{ X } 8.33}$ = 48,000 gallons of cold water required for cooling purposes. Then 48,000 + 2628 = a total of 50,628, or say 50,000 gallons of condensate water to figure on in condensate salt loss.

EFFICIENCY OF EXTRACTORS

"The operators will bring composite samples of the "before" and "extraction" liquor to the laboratory. These composite samples are made up of samples taken every half hour of the operation. The chemist must examine the EXTRACTION RECORD and insist that he be furnished with

the proper samples from each extraction."

PHENOL BEFORE EXTRACTION:

200 cc. of the sample which has been well shaken is diluted to 1000 cc. with water. It is well shaken and a 50 cc. sample taken with a pipette for analysis. This sample is placed in a glass-stoppered separatory funnel and the phenol content is determined by the Tri-Brom-Phenol method. Phenol per Litre = Grs. Tri Brom X log. (9.4538 - 10) X100. Lbs. Phenol per 44,000 gals. = Grs. Litre X 367.

PHENOL AFTER EXTRACTION:

Take 10 cc. of sample and determine phenol as above. Extractor efficiency =

$$\frac{\text{Lbs. extracted}}{\text{Total lbs. before extraction}}$$

TESTS ON C. P. PHENOL

SAMPLES

Three samples are taken from each series, 1 at the beginning, 1 in the middle and 1 at the end of each distillation run.

A composite sample is made from each drum of a shipment. This is a composite of 75 drums.

DISTILLATION

A distillation test is made on a composite of the series samples. It is also made on the shipment composite. Weigh out 108 grams of sample into a 250 cc. distilling flask. Distill sample through an air condenser into a 100 cc. cylinder. Condenser must be approximately 18" long and tilted at an angle of 20-30°. The temperature at which the first drop falls from the end of the condenser is taken as the boiling point.

Distill until 178° is reached and then take cc. reading. This reads directly the percent below 178°. Distillation is continued and the percent below 182° is also recorded. Distill to dry point and record thermometer reading. (At least 90% should distill below 182° C.)

SOLUBILITY

Take 19.6 cc. distilled water and 80.4 cc. phenol. Mix thoroughly in a cylinder

at 25° C. Note whether separation takes place. (It should be completely soluble.)

RESIDUE

Take 5 cc. phenol and evaporate on watch glass using a steam bath. Note color and amount of residue.

COLOR

Color of phenol must be reported.

MELTING POINT

For the melting point of series sample fill a titre tube about one-half full of sample. Use thermometer as agitator and stir gently until sample begins to crystalize. Take temperature after it has become constant. The melting point is determined on each of the three samples.

For the melting point of the average sample use a 300 cc. beaker instead of titre tube. This is the French method.

The melting point must not be lower than 39.5° by titre tube method or 39° by French method.

QUANTITATIVE ESTIMATION of PHENOL

At about the time I was doing the experimental work on the fusions, trouble was experienced concerning the estimation of the phenol in the waste liquors. The Iodine method for estimation of phenol was mentioned in one reference book ("Allen Organic Analysis") at my command but the original work was not at hand. It was necessary then to spend some little time in perfecting the method from a few hints therefrom. The preparation of iodoform from alcohol and Iodine in the presence of $Na_2 CO_3$ seemed to be somewhat analogous. So with this analogy in view I worked on the estimation of the phenol. As in the case of the iodoform, in the presence of $Na_2 CO_3$ the HI (formed) is prevented from eliminating the iodine atom from the iodophenol. Very good checks were obtained in the estimation of doubly distilled C.P. Phenol using carbonate. With the use of caustic the results were invariably low. So far, so good, but when I came to the estimation of any waste or sulphite liquor

I had trouble due to the sulphites present. As the procedure now stands, exercising just ordinary care, very good results are obtainable.

Wilkie writes, "Less than 1 part of phenol per million can be detected, while 4 parts per million gives an immediate indication with iodine. With bromine 1 part of phenol in 44,000 can be detected immediately, and 1 part in 60,000 on standing 24 hours."

METHOD

Phenol, in the presence of a weak alkali, (Na_2CO_3), is thrown down as a light flocculent precipitate of tri-iodophenol with an excess of standard iodine. The solution is then made acid and the excess iodine is titrated with standard sodium thiosulphate. Six (6) atoms of iodine are used up by one (1) molecule of phenol - $C_6H_5OH + 3I_2 \rightarrow C_6H_2I_3OH + 3\,HI$.

Any matter such as SO_2 and H_2S is oxidized with iodine in acid solution before the addition of the weak alkali is made preparatory to the phenol determination.

SOLUTIONS NEEDED

1. N/20 Iodine Solution.
2. N/20 Sodium Thiosulphate Solution.
3. 5% Sodium Carbonate Solution.
4. 1:3 H_2SO_4
5. Starch Solution.

The convenient dilutions and cc's. of N/20 Iodine required are as follows:

NAME	DILUTION	cc's. N/20 I.
Before extraction	50-2000-25	20
After "	50-2000-25	20
Fusion	5-1000-5	20
Crude Phenol	5-1000-5	50

PROCEDURE

Make the dilution and then make up the portion for analysis to about 150 cc. in a 50 cc. ground glass-stoppered bottle.

Add two (2) drops of Methyl-Orange. Make barely acid and add 2 or three drops excess with 1:3 H_2SO_4. Add about 2 cc. of starch solution.

Carefully titrate any SO_2 or H_2S

with the N/20 Iodine solution to a faint blue starch - iodine color. If necessary come back with Sodium Thiosulphate and finish up with the Iodine to the blue starch - iodine color.

After titrating any SO_2 or H_2S add 10 cc. of the 5% Sodium Carbonate solution and a known amount of standard N/20 Iodine from a burrette and allow to stand for about 15 minutes. (Too little Iodine is indicated by pronounced fading of the blue starch-iodine color.) Generally not more than half the added Iodine should enter into the reaction.

Make acid with 2 or 3 cc. 1:3 H_2SO_4 and then titrate excess Iodine with standard N/20 Sodium Thiosulphate solution. The difference between the Iodine added with the alkali and that titrated with the Thiosulphate, equals that Iodine used up by the Phenol.

1 cc. N/20 I = N/20 $Na_2S_2O_3$ = .0007833 gr.Phenol

J.M.Wilkie, J.Pharm., 1903, 17-161

J. Soc. Chem. Ind., 1911, 30, 402.

TRI-BROWN PHENOL - (VOLUMETRIC)

The formation of insoluble tribromophenol, when bromine is added to phenol, is utilized in its analysis.

A standard solution is prepared containing sodium bromide and bromate in proportion of 5 moles to 1 mole, by dissolving Br_2 in hot caustic solution (and boiling off excess bromine). 100 cc. of N/1 NaOH plus 3 cc. of liquid bromine are brought to boil till solution is colorless and then cooled. Add a few drops of NH_4OH to precipitate any iron - Fe $(OH)_3$ and filter - make up to 1000 cc. This solution will be about of N/10 strength - 1 cc. N/10 Br_2 = .00157 grams of Phenol.

$6\ Na\ OH + 3\ Br_2 \rightarrow Na\ Br\ O_3 + 5\ KBr + 3\ H_2O.$

This solution is standardized by adding KI to a known amount of Bromide-Bromate solution, acidifying and titrating the liberated Iodine with standard Thiosulphate solution.

$1\ Na\ BrO_3 + 5\ Na\ Br + 3\ H_2SO_4 \rightarrow$

$3\ Na_2SO4 + 3\ H_2O + 3\ Br_2$

$6\ NaI + 3\ Br_2 \rightarrow 6\ Na\ Br + 3I_2$

PROCEDURE

To a sample of waste liquor of correct dilution (similar to Iodine method) an excess of standard Bromine-Bromate solution is added. The above is acidified in slight excess with dilute sulphuric acid and allowed to stand a half hour after which Sodium Iodide is added and the liberated Iodine titrated with N/10 Sodium Thiosulphate solution. Another sample of the waste liquor, of like dilution, is acidified and titrated immediately with N/10 Iodine solution. The amount of Bromine used on the first sample,minus the Bromine equivalent of the Iodine used on the second sample, is the equivalent of the Phenol content. The method reads well but the results do not check, either on waste Phenol or C. P. material.

TRI-BROM PHENOL METHOD - (GRAVIMETRIC)

Weigh out 10 grams of the solution. If the solution contains any sulphite, acidify with dilute $H_2 SO_4$, then bubble air through it for several minutes to remove free SO_2.

Transfer to a glass-stoppered separatory funnel and add Bromine, drop by drop, shaking after each successive addition. The Tri-Brom Phenol is not completely precipitated until an excess of Bromine is added, so add Bromine until a faint permanent Bromine coloration is produced. Care must be exercised not to get the Bromine on the skin or clothes.

When precipitation is complete, add 10 cc. chloroform and shake vigorously. The Tri-Brom Phenol will be dissolved. The chloroform solution is then drained off into a tared beaker. Two more washes are then made to insure the complete removal of all Brom-Phenol.

The chloroform is then evaporated on the steam bath until traces of white fumes begin to appear within the beaker.

Grams, Phenol = Grams Tri-brom X .284

$$\text{Percent Phenol} = \frac{\text{Grams Phenol X 100}}{\text{Grams sample.}}$$

This method is not good because with average care one cannot obtain good checks. The Tri-Brom is too easily volatilized.

ORGANIZATION - METHODS - LAYOUT

The phenol plant was the largest individual plant of the New Port group, not only in size but in regard to income revenue. Originally the New Port Chemical Works at Carrollville consisted only of the phenol plant but gradually other plants for making intermediates and dyes were added. During the latter part of November, 1918, the phenol plant ceased to operate because its contracts had been fulfilled and its wastes that gradually found way to the lake (Michigan) were becoming a menace to the drinking water in Milwaukee.

On account of the phenol plant being the "pet" plant of the works no money was spared to make it as efficient as possible.

A General Foreman had direct supervision over the plant assisted by an Operation and a Mechanical Foreman. It was the General Foreman that carried on the inter-official business with the higher officials of the works.

The Operation Foreman had charge of

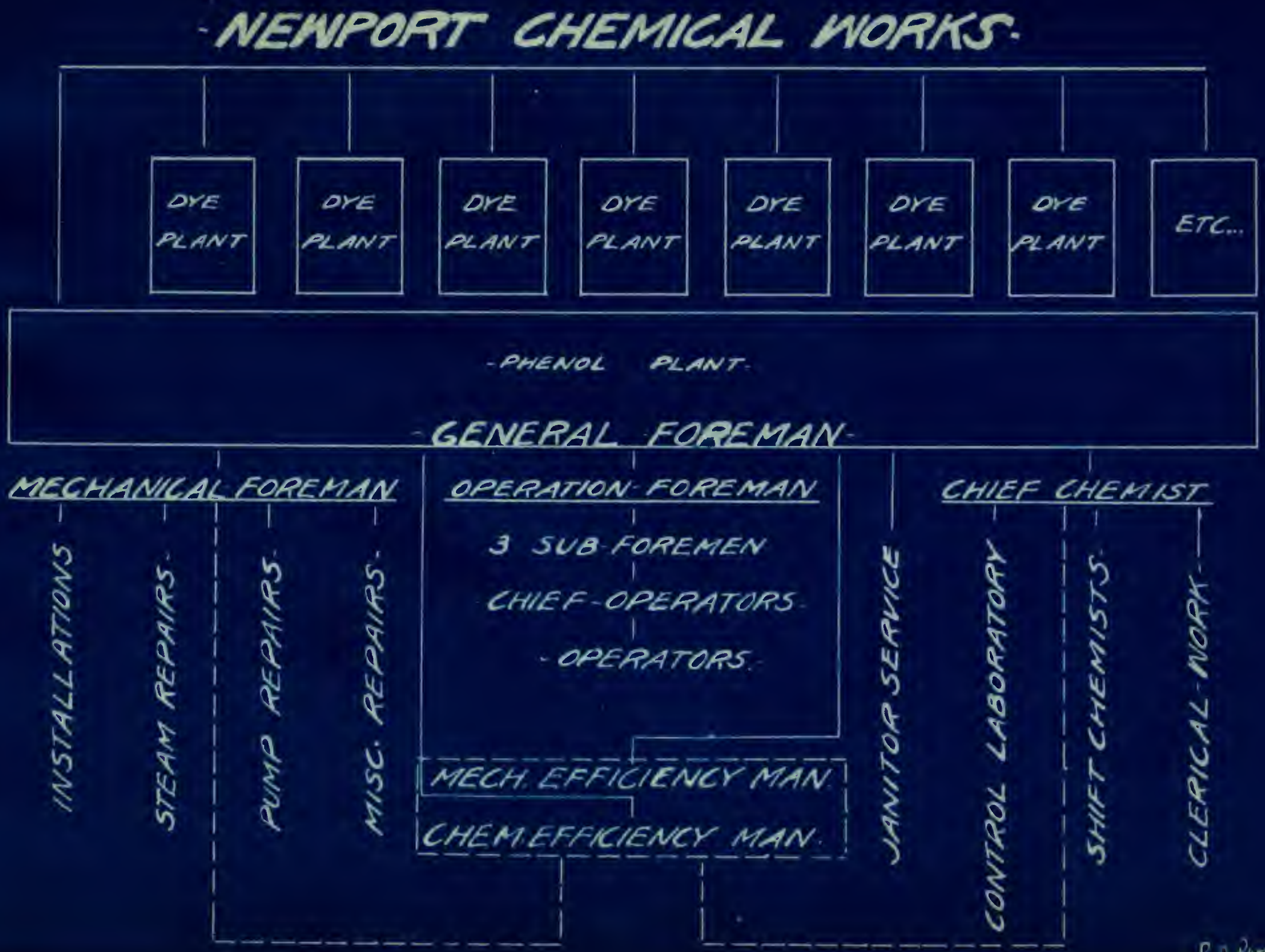
all operation which had to do with the manufacture. He issued orders and directions to three Sub-Formen, one for each of three 8-hour shifts. These Sub-Foremen had direct charge of operation and they in turn had their Chief Operators, who in conjunction with their men performed the operation. The Operation Foreman actually had charge of plant workings. Repairs and changes were made at his suggestions. On the more weighty matters the General Foreman was consulted.

A Mechanical Foreman had complete charge of all mechanical details. Repairs and new installations were executed under his supervision. A pump man and his helpers took care of the upkeep and repairs of all pumps of which there were many. A belt man took care of belts and the oiling of chains and motors. Motor repairs were made on order to and by the Electrical Department of the Works. Pipe and steam fitting repairs were taken care of by a steam fitter boss and his men. All the larger repair work requiring the services of mechanics

and tackle gangs was done on order of the Mechanical Foreman to the Master Mechanic of the Works. Many of the repairs, large and small, were made by daylight. Repairs that were to be made at night were executed by a night repair force operating out of the machine shop.

A Chief Chemist, who was initially responsible to the General Foreman, later to some extent under the jurisdiction of the Operation Foreman, had charge of the control laboratory and of the Shift-Chemists (1 for each shift) whose business it was to watch out for "leaks" and inefficiencies and to keep track of operation in general - the "Watch Dogs", so to speak.

Working hand in hand with each other were a Chemical and a Mechanical Efficiency man. Virtually they were their own managers and responsible to the General Foreman. It was their business to make efficiency tests and to work on inefficient apparatus and processes and make corrections for same. It was as the


NEWPORT CHEMICAL WORKS
DYE PLANT
DYE PLANT
DYE PLANT
DYE PLANT
DYE PLANT
DYE PLANT
DYE PLANT
ETC...
PHENOL PLANT
GENERAL FOREMAN
MECHANICAL FOREMAN
INSTALLATIONS
STEAM REPAIRS
PUMP REPAIRS
MISC. REPAIRS
OPERATION FOREMAN
3 SUB-FOREMEN
CHIEF-OPERATORS
OPERATORS
MECH. EFFICIENCY MAN
CHEM. EFFICIENCY MAN
JANITOR SERVICE
CHIEF CHEMIST
CONTROL LABORATORY
SHIFT CHEMISTS
CLERICAL WORK

R. O. Parrott '19.

Chemical Efficiency man that I served.

Such in a brief way was the personnel of the organization.

The policy of the works was that of "baiting the hook with a dollar". The works being 13 miles distant from Milwaukee with none too good transportation and no accomodations other than fair lunches at cost, it was necessary to offer wages higher than the average. This was especially true concerning the phenol plant, wages ranging from 60 to 75 cents per hour for inexperienced labor while those of the immediate surroundings ranged nearer 30 to 40 cents.

The wage rate varied with the time of employment with the company. At the start a man received a basic wage and after 3, 6, 9 and 12 months he would receive an increase, receiving a maximum wage at one year's resident employment.

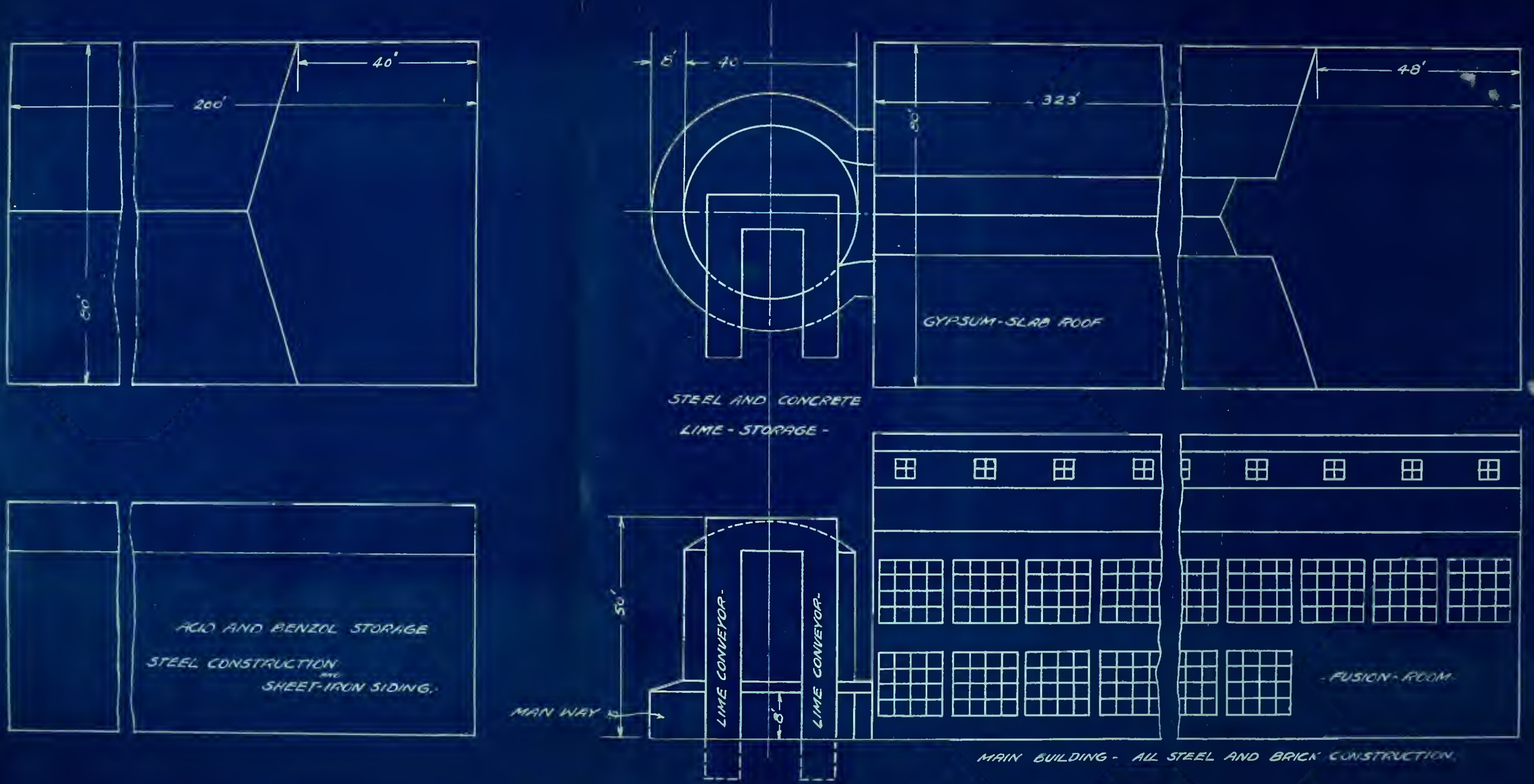
All employes were insured by the Works while in the employ of the same.

Below is a table showing the amount of insurance for the different employes.

Time in Service	Amount of Insurance
3 to 6 months	$ 500.00
6 " 12 "	600.00
1 " 2 years	700.00
2 " 3 "	800.00
3 " 4 "	900.00
4 "	1000.00

Trained men were employed where necessary. The Shift Chemists were college graduates as well as those men in the advanced positions. It was the policy, when possible, to give a man some experimental laboratory experience before putting him in the plant. This procedure offered a man a broader view of the work and made him more valuable, generally.

A close watch was kept on the operation of the plant at all times. Daily reports were made of operation, chemical control, and to the Shift Foremen. This last report gave an idea of the progress of operation from day to day and the Shift Foreman had only to glance at it to get the layout of the operation, not only on his shift but on the others.


40'
200'
80'
8'
40
323'
80'
48'
GYPSUM-SLAB ROOF
STEEL AND CONCRETE
LIME-STORAGE-
ACID AND BENZOL STORAGE
STEEL CONSTRUCTION AND SHEET-IRON SIDING.
50'
MAN WAY
LIME CONVEYOR-
LIME CONVEYOR-
8'
-FUSION-ROOM-
MAIN BUILDING - ALL STEEL AND BRICK CONSTRUCTION.

-BIRD'S-EYE-VIEW-

Inventories were taken every Monday morning and the first of every month, both with the idea of ascertaining the efficiency of operation. The latter was taken with great care, and from this a monthly statement was made. Weekly statements were also made out.

As far as possible the phenol plant was operated on the gravity plan - - See Chart. A central power plant supplied steam for the distillations and power for the numerous motors throughout the plant. Water for general use was pumped from the lake at a central pumping station.

Following is a list of apparatus and labor required for one shift for a plant operating at full capacity with an output of 70 tons of phenol per day. Motors are not listed unless specially fitted.

DAILY REPORT of OPERATION

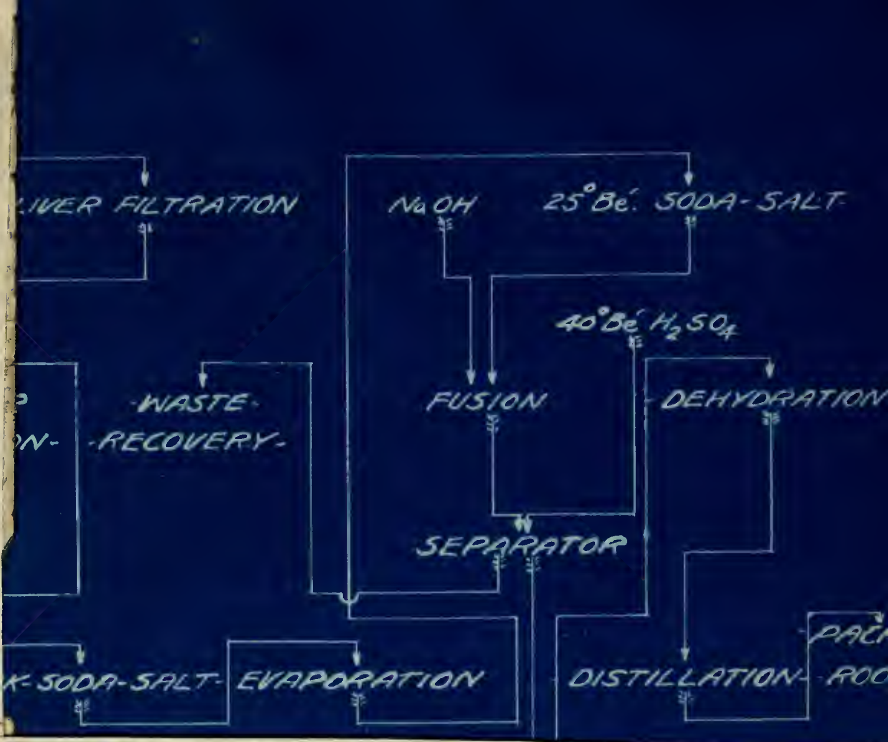
Sulphonations

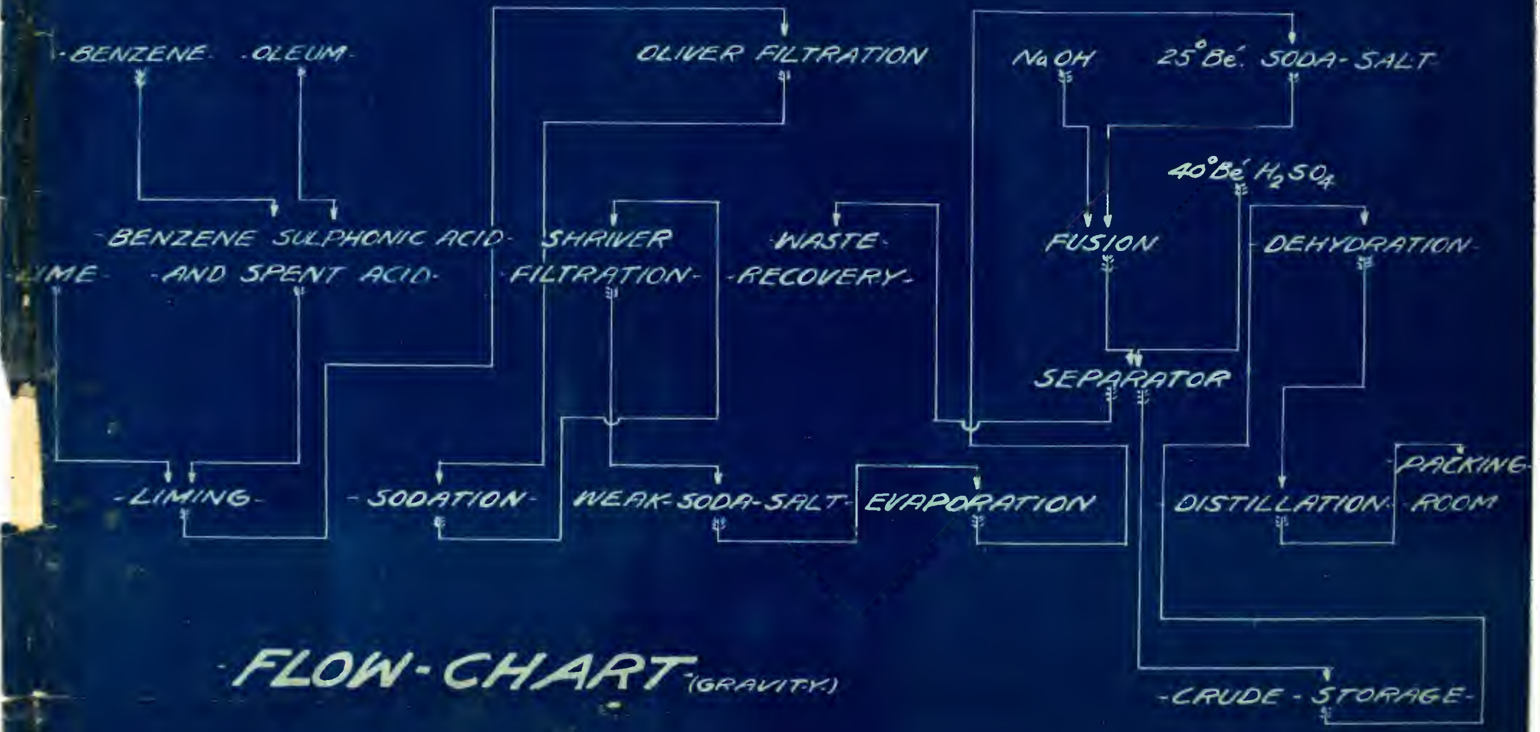
No. Charged - - 35 Dropped - - - 31

Press Operation

No.Sulphonations to Olivers - - - - - - - - -32

No. Soda Presses in Use - - - - - - - - - - 3


IVER FILTRATION
NaOH
25°Be'. SODA-SALT
40°Be' H_2SO_4
P
ON-
WASTE
RECOVERY
FUSION
DEHYDRATION
SEPARATOR
PACK
K-SODA-SALT
EVAPORATION
DISTILLATION
ROO


BENZENE
OLEUM
OLIVER FILTRATION
NaOH
25° Bé. SODA-SALT
40° Bé. H_2SO_4
BENZENE SULPHONIC ACID
AND SPENT ACID
SHRIVER FILTRATION
WASTE RECOVERY
FUSION
DEHYDRATION
LIME
SEPARATOR
LIMING
SODATION
WEAK-SODA-SALT
EVAPORATION
DISTILLATION
PACKING ROOM
CRUDE - STORAGE

FLOW-CHART (GRAVITY.)

R.D Parrott '19.

DAILY REPORT of OPERATION

(continued)

Evaporation (of Soda Salt)

Liquor to - - - 8° Be'. From - - - 24° Be'.

Fusion Operation

No. Charged - - 43 Dipped - - - - - 39

Salt Factor - 1.75 Pounds used 116,440

Separations

No. Made - - - 35

Yield (average) without extraction - - 5.6 in.

" " with " - - 6.2 "

Crude produced - 217 in. In storage -110.0 "

Distillation

Drums (242 Pounds) produced - - - - - - - 193

Still No. 4 Series 1051 Charge 48"

" No. 2 " 1052 " 47"

DAILY CHEMICAL REPORT

Sulphonations

Average Efficiency - - - - - - - - - - - - 95.50%

Benzene Loss .82% Sulphone Loss - .50%

Press Operations

Average Oliver Loss 110# Total - 3520.00#

Average Soda Loss .75 " - 22.50#

Average $Na_2 CO_3$ per sulphonation - - 100.00#

Evaporation

Grams Soda Salt per litre condensate .1435

Separation

Inches of Crude (39.66 gals.) without extractions - - - - - - - - - - - - - - - - - - -5.6"

Inches of Crude (29.66 gals.) with extractions -6.2"

Extractions

Waste Liquor Extraction Efficiency - - 99.3%

Soda Salt - - - - - - - Purity - - - 90.75%

Na_2CO_3 - - - - - 1.76% Na_2SO_4 7.89% Ca0.05%

Phenol Melting Point

Series	1051	1052
M.P.	40.5° C.	40.5° C.
M.P.	40.3° C.	40.4° C.
M.P.	40.6° C.	40;5° C.

DAILY REPORT to the SHIFT FOREMAN

Shift No.	I	II	III
Average Oliver Loss per Sulphonation	120	100	110
No. Sulphonations charged	12	12	11
No. Sulphonations dropped	11	10	10
No. Fusions charged	14	16	13
No. Fusions blown	13	14	12

Remarks: . . . .

Gen.Foreman ________

INVENTORY REPORT

Soda Salt in Process:	Pounds
In Sulphonation Kettles	92,040
" Lime Tubs	13,806
" Soda Tubs	42,000
" Weak Liquor Tubs	90,000
" Evaporator	7,200
" Fusion Room Storage	75,000
Total	320,046

Phenol in Process:	
320,046 lbs. Soda Salt 86,400 Salt in Fusion Kettles	169,487
In Crude Storage	23,000
" Stills	33,000
" Separators	17,000
" Extractors	400
Finished Phenol:	
In Receivers	21,600
Grand Total (Phenol)	264,487

INVENTORY STATEMENT

Raw Material and Yield of Phenol
per pound of Raw Material Consumed.

Dec. 3-9 Inclusive

Pounds of Benzene consumed	607,198.0
" " Caustic "	802,650.0
" " Oleum "	1,241,940.0
" " 60° Acid "	857,200.0
Pounds of Phenol produced	532,500.0
" " " per lb. of Benzene consumed	.88
" " " " " " Caustic "	.66
" " " " " " Oleum "	.42
" " " " " " 60° Acid "	.62

MONTHLY STATEMENT

Total Sulphonations (month) - - - - - - - -	537.0
Average " (per day) - - - - - - - -	17.3
Benzene loss as soda salt per sulphonation in pounds - - - - - - - - - - - - - -	27.0
Sulphone loss as soda salt per sulphonation	30.0
Oliver Press " " " " "	131.7
Total Soda Press loss (month) - - - - - - -	188.7
Average percent loss Benzene per "	.55
" " " Sulphone " "	.61
" " " Oliver Soda "	2.85
" " Sulphonation Efficiency	95.20
" " Soda Salt Operation	92.40
Total Fusions (month)	658.00
Average " (per day)	21.20
Total Separations (month)	645.00
Average (per day)	20.80
" gallons Phenol with extraction	274.50
" " " without "	237.20
" " " of "	37.30
Total gallons crude (month)	174,772.0

MONTHLY STATEMENT

(continued)

Pounds C. P. Phenol (month)	963,750.5
" (average) " per Sulphonation	1,776.0
" " " " Fusion	1,450.0
" " " " Separation	1,478.0
" Benzene used	1,174,800.0

1,174,937 X 1.205 = (Theoretical Phenol) - 1,415,800.0

$\frac{963,750}{1,415,800}$ = percentage overall efficiency - 68.70

Soda Efficiency X Fusion Efficiency = Overall Efficiency.

Therefore -

68.7 ÷ 92.4 = percent Fusion Efficiency - 74.30

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

PLANT EQUIPMENT

No. Pieces	Name of Apparatus	Men
	SODA SALT DEPARTMENT	
24	Sulphonators	3
8	Benzene Weigh Tanks	1
10	Acid Weigh Tanks	
2	Benzene Pump	
2	Acid Blow Eggs	1
2	Sulphonation Montejus	1
2	Gravity Tanks	
8	Lime Tubs	3
4	Lime Mixers	6
2	12-Horse Motor	
8	Oliver Presses & Equipment	5
1	Oliver Heater	
4	Soda Tubs	2
1	10-Horse Motor (for Soda Tub agitation)	
6	Weak Liquor Tubs	
4	Shriver Plate Presses	2
2	Evaporators (35 tons each)	1
1	Nash Centrifugal Compressor	
2	Centrifugal Lime Pump (Oliver)	

PLANT EQUIPMENT

(continued)

No. Pieces	Name of Apparatus	Men
	Soda Salt Department	
2	Centrifugal Oliver Filtrate Pumps	
2	Centrifugal Soda Pumps (Shriver)	
	Fusion Room	
36	Fusion Kettles & Fire Holes	16
12	Storage Tanks)	2
36	Measuring Tanks)	
36	5-Horse Motors (Fusion Kettle)	
2	Direct-Connected Nash-Cent. Compressors	
2	Circulating Tanks	
2	Circulating Pumps (Centrifugal)	
	Separating Room	
15	Separating Tanks	2
5	Waste Pumps (Centrifugal)	2
2	Crude Phenol Storage Tanks	
	Recovery Building	
2	Recovery Units and	
4	Centrifugal Pumps.	1

PLANT EQUIPMENT

(continued)

No. Pieces	Name of Apparatus	Men
	Recovery Building	
3	Condensate Tanks and	
1	Worthington Steam Pump	
3	Storage Tanks (large)	
	Distillation & Packing	
2	Large Dehydrating Stills) (	4
4	Refine Stills and Equipment)	
3	Weigh Scales (Packing Room)	6
	Packing and Barreling Boys	10
	Control Laboratory	
	Chemist	1
	Chemist Helpers	3
	Janitor Service	10
	Pump Man and Helper	2
	Belt Man	1

The raw materials needed to produce 70 tons of Phenol per day would be in round numbers.

Material	Factor	Pounds
Benzene (100%)	(1.13)	158,000
Oleum (10%)	(2.38)	333,000
Caustic (100%)	(1.52)	213,000
60° Be'. H_2SO_4	(1.61)	225,000
Lime	(1.265)	177,000
Soda Ash (98%)	(.0565)	8,000
	Total Pounds -	1,114,000

If for instance an average railroad car load is 30 tons, then 19 cars would be required every 24 hours to handle the raw materials to keep a 70-ton-a-day phenol plant in operation.

MISCELLANEOUS DATA

2100 pounds of Benzene by weight takes 2637 pounds of 100 percent Sulphuric Acid but practically requires 1954 pounds in excess, or 4590 pounds total -

2100 lbs. of Benzene are equivalent to the following: (theoretically)	4252 lbs.	$C_6H_5SO_3H$
	4845 "	$C_6H_5SO_3Na$
	4763 "	$(C_6H_5SO_3)_2Ca$
	1456 "	$Ca(OH)_2$
	1102 "	Ca O
	3122 "	C_6H_5ONa
	2531 "	C_6H_5OH
	2150 "	NaOH
	1426 "	Na_2CO_3
	1345 "	$CaCO_3$

To acidify 3122 lbs. of C_6H_5ONa there are required.	1319 lbs.	100% H_2SO_4
	1700 "	60° Be'. H_2SO_4
	2740 "	40° Be'. "

1954 lbs. of excess Sulphuric Acid requires the following to neutralize.	1476 lbs.	$Ca(OH)_2$
	1088 "	Ca O.

1476# Ca $(OH)_2$ = 1088# CaO = 3430# $CaSO_4.2\ H_2O$

Theoretically = [illegible]

2.25 pounds Soda Salt requires 1 pound of Caustic for the fusion.

Lbs. Benzene X 2.308 = lbs. of Soda Salt

" Soda Salt X .5222 = " " Phenol

" Benzene X 1.205 = " " Phenol

Specific gravity of 80 percent crude at (21° C.) = About 1.08.

Specific gravity of C.P.Phenol = 1.06 at 33° C.

J. Soc. Chem. Ind Vol. 37-16-269 quotes:

"..................... Perkins values (J. Chem. Soc. 1896-69-1182) can only be obtained after suitable purification and drying. .... Boiling point of the middle fraction = 182.5° C. This fraction further dried over Calcium Chloride (ignited) for several hours gave a resulting phenol of M.P. of 40.5° C. ....."

Percent H_2O	Percent C_6H_5OH	M.P.
0.00	100.00	40.5
.03	99.97	40.45
.33	99.67	39.20
.63	99.37	38.00
.93	99.07	36.80
1.23	98.77	35.70
1.53	98.47	34.50

Percent H_2O	Percent C_6H_5OH	M.P.
1.83	98.17	33.45
2.13	97.87	32.50
3.68	96.32	27.50
5.35	94.65	22.80
7.23	92.77	18.50
9.49	90.51	14.20
12.30	87.70	10.70

At New Port the melting point of still batches ranged from 39.5 to 40.5° C. The boiling point ranged from 180 to 182° C.

New Port Phenol, if allowed to stand around exposed to the air, turned pink to red in color, but if sealed air-tight it remained colorless. This coloring is attributed to many different causes such as copper, iron, benzoic acid, etc.

The End